CHARACTERISATION AND DEGRADATION STUDY OF HISTORIC POLYOLEFIN GAS PIPES

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Declaration

This is to certify that the material contained in this thesis has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

Naima Zodros

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Abstract

Polyethylene (PE) pipes are widely used by the water and gas industries to reline or replace corroded or leaking mains. PE pipe systems are designed on the basis of a 50-year service life.

Polyethylene gas pipes were first introduced to the UK in 1969. Changes within the additives package of these new materials were frequent from this date. The additives package would also vary within the same material grade during manufacturing. This would lead to changes in the general properties of the PE pipes such as their pressure bearing capacity.

The MSc thesis relates to work carried out on historic medium and high-density polyethylene gas pipes after almost 50 years of service. The work involves identification of the polyolefin grade used for these gas pipes and the study of their remaining lifetime. The project presents and discusses the results of an in-depth investigation into the characterisation and the degradation of the exhumed pipes. The degradation has been studied using Fourier Transform Infra-Red (FTIR) and Differential Scanning Calorimetry (DSC). The identification work was conducted using DSC, Melt Flow Rate (MFR) and density measurements.

The exposed outside surfaces of the polyethylene pipes (the remaining faces of the samples were masked with silicone elastomer) were aged in water at various temperatures. The depletion of antioxidants from the exposed face as a function of ageing time in water was monitored by conducting Oxidation Induction Time (OIT) of thin samples cut from the exposed face. Previous work showed that this relationship could be used to predict the residual lifetime of a modern blue PE100 water pipe[1]. However, this was found to be untrue for the historic gas pipes, due to the high variability of OIT results before exposure masking / confounding any potential changes.

Medium and high-density PE were differentiated using well established analytical methods such as MFR and density. The medium-density Polyethylene grades were differentiated using a recently introduced DSC technique known as Stepwise Isothermal Segregation (SIS) which was performed on the DSC instrument. In this study the sample mass normalised SIS data was treated in a novel way in attempt to simplify the data. The method involved taking the first derivative of the sample mass normalised SIS data. This approach led to improved resolution of crystal structures of differing lamellar thickness than possible using the original sample mass normalised SIS data. The SIS technique was proven

to be an efficient identification technique. It was possible to obtain reliable fingerprints for each type of PE and material grade using this technique.

The degradation study conducted on the unexposed old gas pipe materials using OIT, and FTIR indicated that significant amounts of antioxidants were still remaining in the pipe. However, as assessment of the mechanical performance was beyond the scope of this study, it is not possible to confirm that these old pipes are still fit for service. The OIT data for samples taken around the circumference of the pipe showed a high level of variability as did OIT data for samples taken along the length of the pipe. This variability in stability clearly indicates very poor distribution of stabilisers during manufacture and probably points to early use of a rudimentary masterbatch. Therefore it was not unexpected that the variability in OIT data was even higher after hydrothermal ageing. The scatter in the data was so severe that it was not possible to determine the residual lifetime of the pipes.

Contents

List of symbols and abbreviations

Å	Ångström
Atm	Atmosphere
cm	Centimetre
CRB	Cracked round bar
DSC	Differential scanning calorimetry
F	Fahrenheit
g	Gram
GPC	Gel permeation chromatography
HAS	Hindered amine stabilizers
HALS	Hindered amine light stabilizers
HDPE	High density polyethylene
ICI	Imperial chemical industries
K	Kelvin
kj	Kilojoule
LDIW	Low ductility inner wall
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
FTIR	Fourier transform infrared
MDPE	Medium density polyethylene
MFR	Melt flow rate
mg	Milligram
min	Minutes
nm	Nanometre
mol	Mole

List of abbreviations

OIT	Oxidation induction time
PE	Polyethylene
RPM	Rate process method
SCG	Slow crack growth
SIS	Stepwise isothermal segregation
TGA	Thermogravimetric analysis
T_m	Melt temperature

1 INTRODUCTION

1.1 Aim and objectives

The aim of this this project is to find an efficient way to identify pipe materials in service and to find a residual lifetime determination technique for the Aldyl A material. This goal will be reached through the completion of a series of objectives.

The identification of Aldyl-A grade material will be completed using established techniques such as MFR and density but also using one modern technique called SIS. The manufacturing date of the pipe which may also help the classification will be taken directly on the pipe

The pipe exhumed will be submitted to OIT and FTIR analysis to find out if they are still fit to service.

OIT values for the hydrothermally exposed pipes will be plotted against exposure time in the hope to find a linear relationship from which the remaining lifetime of the Aldyl A material will be extrapolated.

1.2 Summary

Polyethylene (PE) pipe has been used for the distribution of gas since 1969 because of its flexibility, long term stress crack resistance and weldability. As a result, the pressures that the pipe can resist decrease with time and this leads to premature failure. In practice, PE pipes may fail in a brittle or ductile fashion. Brittle failures occur due to inherent defects, which, under load, eventually form a crack, which grows with time. Ductile failures occur usually when the pipe has been impaired or over pressurised.

PE pipes have a 50 years lifetime requirement and the first generation PE gas pipes are now reaching the end of their design lifetime. There is a strong interest for Utility Companies, which are responsible for managing these assets, to find out about the remaining lifetime of these “old” materials.

In order to respond to this requirement, it is proposed that a methodology is

developed to predict the remaining lifetime of old PE gas pipes that have been produced from a specific grade resin (Aldyl A). Therefore the different types of PE and their properties would be investigated. The degradation mechanism for PE will be studied in order to decide on the lifetime determination method for the old Aldyl A PE resins.

The test normally used to assess the suitability of old and new material is known as the stress regression test[2]. The test involves the application of internal pressure to the pipe until rupture occurs. The results of the short-term tests are used to predict long term response. International standards[2] require testing for periods of over one year and therefore necessitate significant investments in time. It is also possible to determine when a failure is more likely to happen by assessing if the stabiliser package has being consumed. This can be done by monitoring the remaining amount of antioxidant left in the pipe using the OIT technique.

The specific grades of material in early gas pipes introduced in the UK from 1969 were featuring different pipe colours. MFI and density values for these different grades were recorded. Using this information on the material, it was possible to identify the different grades. The DSC instrument was used to run a relatively new technique known as Stepwise Isothermal Segregation (SIS). This technique was introduced as a further stand-alone identification technique, and verified against the identification acquired using MFR and density. SIS allows indirect assessment of the chain fraction that generates a high rate of tie molecules.

The degradation study was lead to understand if the pipe materials had reached the end of their design lifetime where polymer degradation is dominant. During polymer degradation, chemical degradation happens freely and by-products of degradation are created. Some of these by-products contain carbonyl peaks that can be detected via FTIR analysis. At the end of the study, it was concluded that most of the MDPE materials had not reached this stage and thus were still in good condition. FTIR results were discussed for pipe materials that were showing sign of carbonyl peaks. The peak exhibited on the FTIR spectra may be showing additives instead of oxidative degradation products.

As the additive package would vary between and within grades of PE, the variability within the composition for these materials was questioned. The variation

would affect the OIT results after ageing and therefore, would prevent the residual lifetime determination. Extensive work was conducted on old PE pipes to understand the degree of variability in their composition prior to the ageing work.

1.3 History of polyethylene

Polyethylene $(CH_2)_n$ was first synthetized by Hans von Pechman in 1898 during a condensation reaction involving the decomposition of diazomethane.

Commercial Polyethylene was then produced in 1933 by ICI (Imperial Chemical Industries) using a high-pressure free radical polymerisation process. The process resulted in creating a high degree of chain branching leading to the formation of a low-density material with poor mechanical properties which prevented it from being used in high stress applications[3,4,5].

The introduction of the Ziegler-Natta and Phillips polymerisation processes allowed production of more linear molecules with much less chain branching, therefore resulting in higher density and superior mechanical properties. These processes allowed the use of lower temperatures and pressures facilitating the production of a superior PE material. The high-density polymerisation processes could be modified by the controlled addition of comonomers such as butane, hexane and octane.

Linear Low Density Polyethylene (LLDPE) was developed in the late 70s. LLDPE featured properties and structure which were intermediate between the high pressure and low-pressure materials.

In the 1990s, polyethylenes produced with metallocene single site catalysts were commercialized and non-metallocene single-site catalysts were discovered by Brookhart and coworkers[4].

1.4 Types of polyethylene, processes and degradation mechanisms

1.4.1 Polyethylene types

Polyethylene is categorised into various types based mostly on its density and branching. The extent and type of branching as well as the crystal structure and the molecular weight of PE have a significant effect on its mechanical properties. The most commercialised polyethylene grades are HDPE, LLDPE and LDPE.

LDPE pipe products were used in the 1950s for potable water pipes while HDPE pipes were used in the low-pressurized gas network. In the late 1970s gas and water, industries started using MDPE over LDPE. Since 1976, improved versions of HDPE are used for both water and gas industries.

1.4.1.1 Low density polyethylene

Low density polyethylene (LDPE) is only produced by free radical polymerization of ethylene initiated by organic peroxides or other reagents that easily decompose into free radicals[6]. LDPE density is typically 0.915-0.930 g/cm^3. LDPE is the most easily processed of major types of polyethylene and is highly branched and contains relatively high amorphous content which results in outstanding clarity in film for food packaging, a major application. A representation of LDPE is shown in Figure 1.

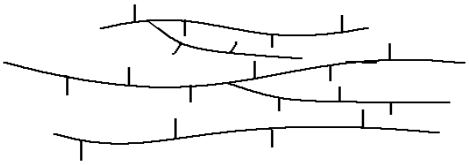


Figure 1. Schematic representation of the architecture of LDPE[9]

1.4.1.2 Linear low density polyethylene

Linear low density polyethylene (LLDPE) features a lower concentration of

branches then LDPE. The branches are short alkyl groups in LLDPE whereas they consist of ethyl and butyl groups in LDPE. The density usually ranges from 0.925 to 0.940 g/cm^3 for LLDPE. The commercialisation of LLDPE has increased in the past 25 years becoming the most produced type of Polyethylene[7,8]. A representation of LLDPE is shown in Figure 2.

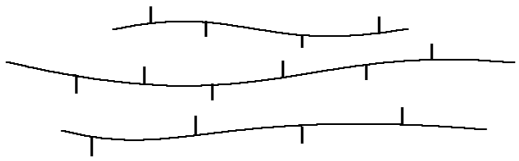


Figure 2. Schematic representation of the architecture of LLDPE[9]

1.4.1.3 High density polyethylene

High density polyethylene (HDPE) is chemically the closest in structure to unbranched polyethylene. HDPE is produced by polymerization of ethylene using Ziegler-Natta or supported chromium ("Phillips") catalysts and it cannot be produced by free radical polymerization[6]. Small amounts α-olefin co-monomers (alkene with double bond at the primary position) are added in many of the commodity grades to establish low concentrations of short chain branching, principally to boost processability but also to improve toughness and environmental stress crack resistance. HDPE has high modulus, yield and tensile properties compared to LLDPE and MDPE. Because of its higher crystallinity, HDPE cannot match the clarity of LDPE, it is harder and more opaque and can resist fairly higher temperatures. HDPE density range is typically 0.940-0.970 g/cm^3. A representation of HDPE is shown in Figure 3.

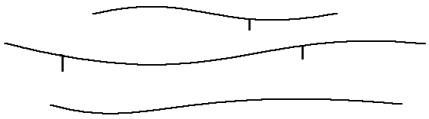


Figure 3. Schematic representation of the architecture of HDPE[9]

HDPE is widely used in extruded pipe for potable water and gas distribution. It is also very important for application such as blow molded packaging for household

and industrial chemicals (i.e: bottles for bleach, shampoo, detergent, etc).

1.4.1.4 Medium density polyethylene

Medium-density polyethylene (MDPE) is produced by copolymerization of ethylene with α-olefins using Ziegler-Natta, supported chromium or single site catalysts. MDPE cannot be produced by free radical polymerization[6]. MDPE has a linear structure similar to LLDPE, but its comonomer content is lower. MDPE is characterized by a density range of 0.926–0.940 g/cm^3 which is less dense than HDPE. It also is less notch sensitive than HDPE. Stress cracking resistance is better than that of HDPE. MDPE is used in geomembrane and pipe applications, such as gas distribution.

1.4.1.5 Bimodal improved polyethylene resin

Bimodal PE technology was developed in Asia and Europe in the 1980's using the metallocene process. High performance bimodal materials with a bimodal molecular weight distribution have a unique combination of the highest pressure rating for a PE (PE100) material as well as an exceptional resistance to SCG[10] (slow crack growth) and excellent resistance to RCP (rapid crack propagation).

Higher molecular weight fractions lead to mechanical strength whereas lower molecular weight fractions enhance flow properties and polymer processing. As a result, polyethylene materials with wide molecular weight distribution were able to provide a better balance of properties. The combination of good mechanical properties and easier processing was reached with the introduction of a bimodal resin[10].

1.4.2 Polymerization processes for polyethylene

1.4.2.1 High pressure polymerization

The compression process was the first method developed for the synthesis of polyethylene by ICI, in Britain, in the 1930's. They discovered that ethylene gas could

be converted into a white solid by heating it at very high pressures in the presence of minute quantities of oxygen. The reaction was carried at a pressure between 1000 and 3000 bar and a temperature of 80 to 300ºC, either in a tubular reactor or an autoclave[11].

The technique was presenting formidable mechanical problems and a large power requirement[11]. The polymerisation reaction was relatively random and led to the synthesis of a wide range of molecule size giving rise to LDPE, see in Figure 4.

By controlling the reaction conditions, it was possible to select the average molecule size (or molecule weight) and the distribution of sizes around this average (molecular weight distribution)[11]. The chains were highly branched (at intervals of 20 – 50 carbons). Subsequent experiments proved that pressure was a key factor in the synthesis of polyethylenes of different molecular weights[11]. Keeping the temperature in a range of 200ºC while decreasing the pressure resulted in the formation of higher molecular weight polymers[11]. Figure 5 shows the molecular weight distribution and the short chain branching for HDPE.

Figure 4. Molecular weight distribution for 'high pressure' LDPE[9] and formation of long chain branching

Figure 5. Molecular weight distribution for 'low pressure' HDPE[9] and formation of short chain branching

1.4.2.2 Ziegler process

Ziegler process is an industrial process for the manufacture of high-density polyethylene introduced in 1953 by the German chemist Karl Ziegler. It allowed the manufacture of polyethylene at lower temperatures and pressures than used in the original process.

In general, Ziegler polymerisations are run under an inert atmosphere such as nitrogen, usually in hydrocarbon diluent at moderate temperatures (50-120 ºC) and moderate pressure (1 atm to 10-20 atm). They can be carried out in gas phase, in slurry, or in solution. The particular conditions used are dependent on the catalyst, on the nature of the product and on the nature of the diluent.

The original Ziegler-type processes are based on catalyst made from aluminium alkyl, especially alkyl aluminium chlorides, combined with $TiCl_4$[12]. With the development of these catalytic systems it was possible to produce polyethylene with molecular weight as high as 3,000,000 with lower temperatures and pressures (temperatures below 100ºC and pressures of less than 100 atm).

1.4.2.3 Phillips process

The Phillips process was developed at the same time as the Ziegler process. It is a process for making high-density polyethylene by polymerizing ethane at high pressure (30 atm) and 150°C but using a chromium oxide catalyst[4]. Like the Ziegler process, the polymerization can be carried out in the gas phase, in slurry, or in solution.

1.4.2.4 The standard oil process

The standard oil process is based on the use of molybdenum oxide under moderate conditions of temperature and pressure. The process was developed to compete with the Phillips process but was never as efficient.

1.4.2.5 Metallocene process

When metallocene catalysts were discovered in the late 80s, they allowed producers to refine and even design the structure of polymers. Metallocene catalysts are based on transition metals of group IV such as titanium and zirconium – as with Ziegler catalysts – incorporated into a cyclopentadiene-base structure with two alkyl, halide, or other ligands and co-catalyst, methylealuminoxane (-MeAlO-) commonly known as MAO[4]. However the Metallocene process differs to the Ziegler method because well-defined single catalytic sites and well-understood molecular structures are used. Each catalyst contains only one type of active site, all of them polymerizing the available monomers in an identical fashion leading to a uniform product with a predictable and homogeneous weight distribution[3].

1.4.3 Molecular structure of polyethylene

Polyethylene results in a sequence of ethylene monomers connected together by chemical covalent bonds in which the bonding electrons are shared equally between the bonded carbon atoms.

The Linear polyethylene molecules possess a considerable degree of

flexibility. The single covalent bond connecting two carbon atom can rotate. The ease or frequency with which rotations occur in molecules depends on the height of the rotational energy barriers in relation to the thermal energy possessed by the molecules and is therefore temperature-dependent. As a result of random thermal motion (Brownian Movement) of the polymer chain segments, the conformation of an individual molecule changes at a rate depending upon the inherent rotational energy barriers of the polymer, as well as upon the environmental factors such as temperature or imposed mechanical stress.

Although the end groups of the macromolecule might not be identical, a sufficient level of chemical and geometric regularity is created through the molecule so that crystalline region (crystallites) may appear. The average length of the polymer chains often exceeds the size of the crystallisation nuclei resulting in partial crystallisation. The same molecule may participate simultaneously in crystallite growth at different points along its length. The molecule motion becomes seriously hindered as crystallisation occurs and it becomes more difficult, for non-crystallised portions of the molecule to enter a crystal lattice.

1.4.3.1 Structural model

In the solid state, the polymer molecules are twisted around each other however; in the molten state the molecules arrange themselves in a random coil configuration. X-ray diffraction of ideal crystallised polymer samples has always shown a combination of crystalline and amorphous patterns[13]. This led to the conclusion that the partially crystallised polymer contains very small crystals embedded in an amorphous matrix. This concept is called the “fringed micelle” and it assumes that there is a random arrangement of long linear macromolecules which, in regions of sufficient chain alignment, are able to form a crystal lattice[14].

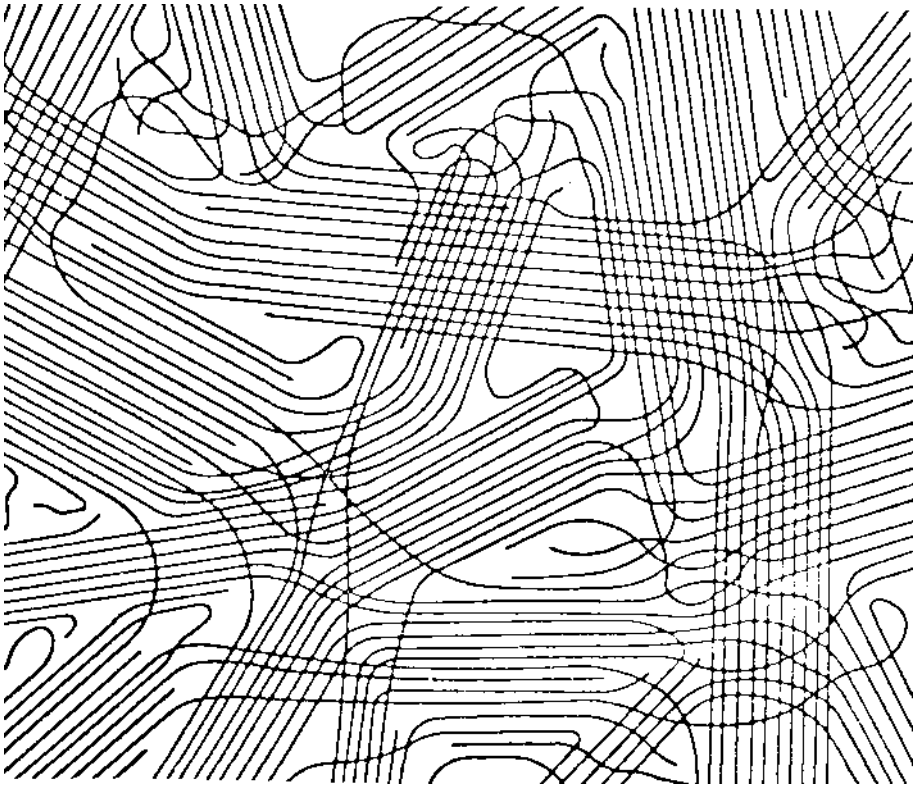


Figure 6. Fringed micelle[15]

Developments in morphology became possible through the introduction of linear polyethylene. Linear polyethylene is known to precipitate from solution to form single crystal lamellae. The lamellae crystal is the basic morphological unit in semi crystalline polymers[16,17,18]. Crystals of this type were found to be of the uniform thickness of 100 angstroms, suggesting the formation of layers. However, the average chain length could be a few thousands angstroms long. Electron diffraction work has shown that the chains were aligned perpendicular to the lamaellar surface. It was deduced that the chains must fold back and forth numerous times across the layer to allow this kind of organisation.

In melt crystallisation, the lamellae can be considered as only part of a large scale structure of which can be readily seen using polarising microscopy[18]. These larger scale entities are well known and named spherulites. The banded spherulite is a common form seen in PE and displays concentric rings identified by Keller[19]. Chain folding has been adopted as the general mode of crystallisation amongst all flexible chain polymers. The schema of a spherulite is shown in Figure 7.

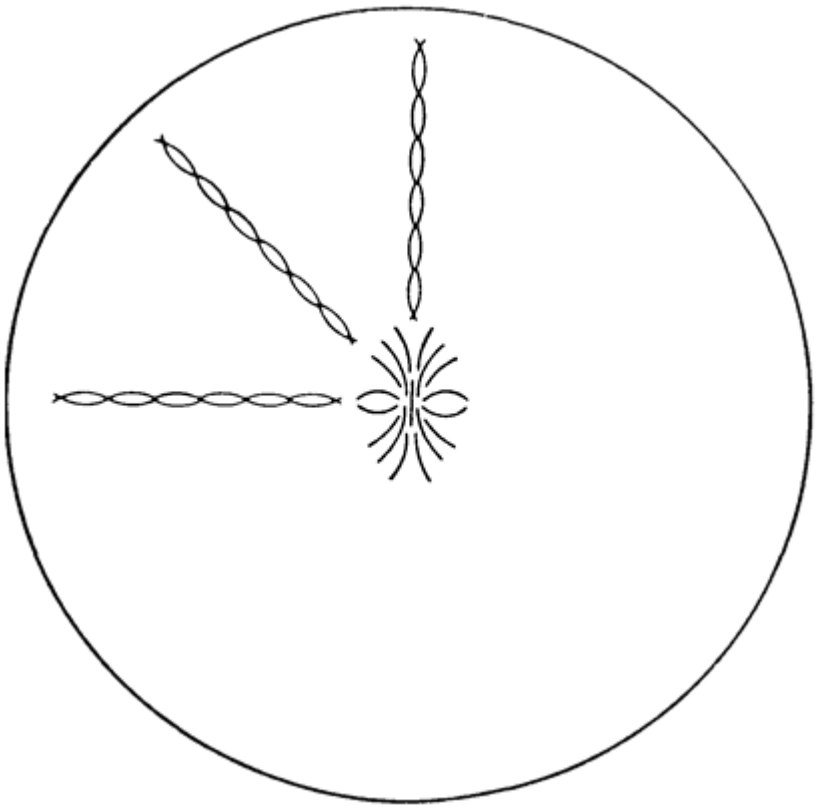


Figure 7. Schema of a spherulite[15]

1.4.3.2 Fringed micelle concept

The model assumes that the polymer is a non-stationary two-phase, system. In the amorphous phase, the formation of a stable crystalline phase is avoided as one polymer molecule is generally involved in several crystals. The small crystallites act as physical cross-links and are responsible for the shape of the sample. The fringed micelle model developed for semi crystalline polymer suggested that the molecular chains formed region of order (crystallites) and disorder (amorphous regions)[20].

1.4.3.3 Folded chain concept

The concept of chain folding came from the discovery of spherulites together with the discovery of crystalline lamellae of a thickness of approximately 100 Å. The individual polymer molecules locked in a crystal are folded back and forth upon themselves.

X-ray evidence[21] indicates that the polymer chains are arranged with their axes perpendicular to the principal faces of the crystal or parallel to its thinnest dimension usually in the order of 100-200 Å. This length represents only a small fraction of the total length of a high polymer chain. Therefore, the molecule is assumed to be folded into the crystal platelet. The crystal thickness is characterized by the folding length of the polymer molecule, which depends on the temperature at which the crystallisation has taken place. Folds are occurring at regular intervals along the chain and are dictated by thermodynamic considerations. A diagrammatic representation of chain folding is shown in Figure 8.

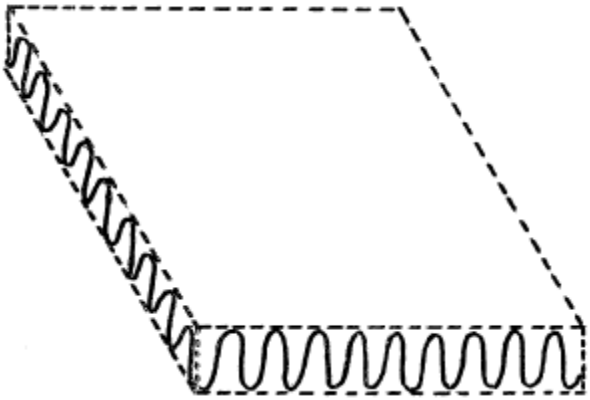


Figure 8. Schema representing chain folding[15]

Loose chain portions and cilias are portions of the polymer chain that stay excluded from the folding pattern[22]. Schematic representations of cilia formation and loose loops are shown in Figure 9. The loose cilia can become incorporated in consecutive overlying layers to constitute the tie molecules. The occurrence of a branch at a near and intended fold point on the polymer chain should result in a dislocation at that point because the chain could no longer fold in the manner necessary to accommodate itself into the crystal. As a result, the remainder of that chain would be excluded from the crystal into which part of its length has already been incorporated. If the excluded portion is of sufficient length and appropriate constitution it can accommodate itself into another nearby crystal. These two crystals would then be tied together by the primary valence bonds of the polymer chain. Repetition of this process lead to a crystalline mass securely interconnected by polymer chain bridges and is characterised by superior properties. This concept accounts for the superior mechanical properties of crystalline polymers. It is

substantiated in practice by the remarkable increase in creep resistance bestowed upon otherwise linear ethylene polymers by the branches introduced through copolymerisation with minor amounts of butene or hexene[23].

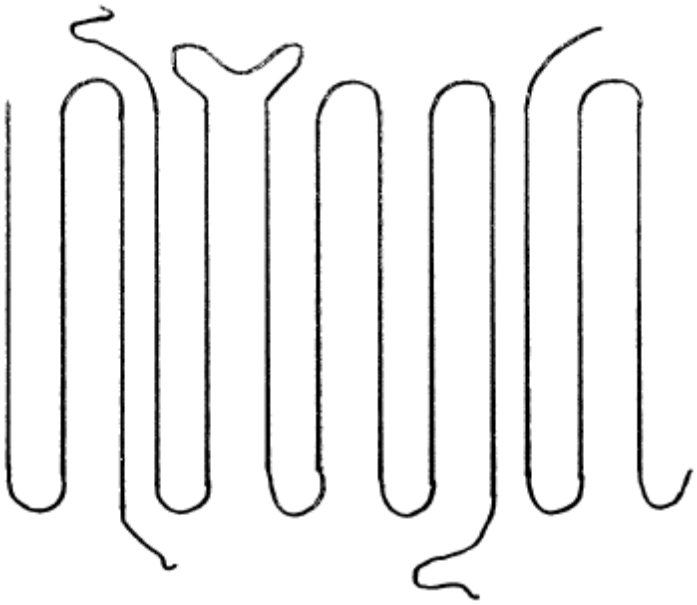


Figure 9. Schema representing cilia and loose loops[15]

1.4.4 Degradation of polyethylene

1.4.4.1 Auto-oxidation of polyethylene

Oxidative degradation takes place for PE of all levels of crystallinity and molecular weight. The crystallinity is linked to the density of the polymer and the molecular weight is linked to the melt index[24].

Amorphous zones of PE are oxidized first as they are more accessible to oxygen molecules than densely packed crystalline regions.

Hydroperoxides are the primary products of polyalkene oxidation[24]. Secondary products are oxygen-containing compounds that result from the decomposition of hydroperoxides. Degradation of polyalkene in oxygen begins via an initiation step which generates the radical precursors:

(1) $RH \rightarrow R\cdot + H\cdot$

Temperature, UV radiation, mechanical treatment and/or chemical factors such as traces of initiators such as peroxides and hydroperoxides can induce initiation. During the propagation step showed in reaction (2), oxygen comes in contact with the newly formed chain radical (R·) and create a peroxy radical intermediate. .

(2) $R\cdot + O_2 \rightarrow ROO\cdot$

Peroxy radicals are extremely reactive. They can easily extract labile hydrogens from polymer molecules to generate hydroperoxide species. They can also bind with other polymer radicals to create unstable species through which the process can continue.

(3) $ROO\cdot + RH \rightarrow ROOH + R\cdot$

When the oxidation process is advanced, initiation happens with a higher occurrence due to the decomposition of hydroperoxides forming radicals through monomolecular (4) or bimolecular reactions (5) and (6). The propagation results in the chain oxidation of polyalkenes that leads to chain branching. Chain Branching is characterised by the formation of stable oxygen-containing polymer and low-molecular-mass compounds.

(4) $ROOH \rightarrow RO\cdot + \cdot OH$

(5) $2ROOH \rightarrow RO\cdot + ROO\cdot + H_2O$

(6) $ROOH + RH \rightarrow RO\cdot + R\cdot + HOH$

Labile hydrogens of the polymer can be easily extracted by the alkoxyl radical RO· and also by the hydroxyl radical HO·.

(7) $RH + RO\cdot \rightarrow ROH + R\cdot$

(8) $RH + HO\cdot \rightarrow H_2O + R\cdot$

Termination of the kinetic chain of oxidative degradation of polyalkenes is attributable to the reactions:

(9) $2R\cdot \rightarrow RR$

(10) $2ROO\cdot \rightarrow ROOR + O_2$

(11) $R\cdot + ROO\cdot \rightarrow ROOR$

(12) $R\cdot + RO\cdot \rightarrow ROR$

For polyethylene oxidation, Luongo (1960)[25] reported that ketones were the major oxidation products with per-acids and per-esters as the minor products.

1.4.4.2 Thermo-oxidation

The processing techniques employed to produce pipe system components lead to considerable changes[26] in physical and chemical properties. Such techniques are known as extrusion for pipes and injection moulding for fittings. Thermo-oxidation can also happen during end-use application[27].

Thermo-oxidation leads to chain scission and cross-linking within the polymer. Thermo-oxidation, favoured during processing is triggered by hydroperoxides[28, 29, 30, 31] which are intermediates of the oxidation process. Hydroperoxide decomposition leads to the degradation of the polymer due to the radical species formed in its decomposition. Radical species, which are in this case alkyl, peroxy, alkoxy and hydroxyl radicals affect melt processing, long-term stability and UV stability.

Formation of radicals through bimolecular (5 and 6) and monomolecular (4) reactions are most likely to happen under elevated temperatures. Monomolecular reactions will become dominant with increasing temperature because their activation energy is significantly higher than that of the bimolecular reaction31.

During end-use application, hydroperoxydes will also lead the oxidative degradation of polyethylene.

1.5 Stabilisation routes

Stabilisers are required to adverse the effect of the degradation resulting during the processing, fabrication, storage and service conditions.

1.5.1 Phenolic antioxidants

Phenolic antioxidants are the most used stabilizers for polymers. When hindered, the phenol groups act as free-radical scavengers to prevent or interrupt oxidation reactions[32]. The steric hindrance due to bulky substituents in the 2- and/or 6-position influences the stability of the phenoxy-radical or the mesomeric cyclohexadie-nonyl-radicals. Bulky substituents stop the reaction between the phenoxy radical and the polymer and also inhibit dimerization of two phenoxy radicals.

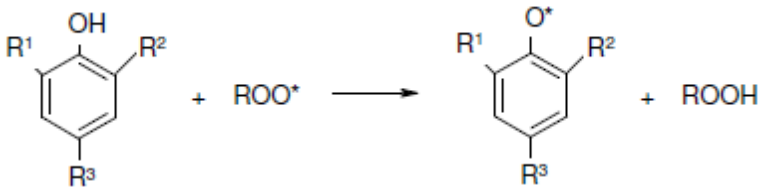


Figure 10. Phenolic antioxidants action mechanism[32]

1.5.2 Amines antioxidants

Secondary aromatic amines and aromatic diamines are extremely efficient H-donors[32]. However they generate various coupling products which discolor the polymer, therefore they are essentially destined to black filled polymers such as rubbers.

Sterically hindered amines are designated as Hindered Amine Stabilizer (HAS) and as Hindered Amine Light Stabilizer (HALS). To prevent the oxidation of the polymer it is important that nitroxy radicals (NO·) are generated. Unfortunately, the mechanism of nitroxy radical formation and the function of nitroxy radicals are controversial in the literature.

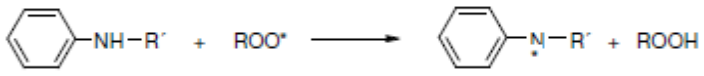


Figure 11. Amines antioxidant mechanism[32]

The nitroxy radical once formed can react with an alkyl radical to create hydroxylamine ether (NOR). The hydroxylamine ether then reacts with a peroxy radical (ROO·) resulting in the formation of alkyl peroxide (ROOR) and the

regeneration of the nitroxy radical. The oxidation of hydrocarbons still happens when HAS is involved, therefore it is important to stabilise the polymer with the appropriate melt stabilization.

1.5.3 Phosphite antioxidants

Hydroperoxide decomposers can prevent the homolytic split of the hydroperoxide group into reactive RO· and ·OH. Organophosphorous compounds are efficient hydroperoxide decomposers[32]. They are in conjunction with hydrogen donor primary anti-oxidants. Phosphites and phosphonites allow stabilisation through three mechanisms. First there is the decomposition of hydroperoxides, then reactions with peroxy radicals and finally with alkoxy radicals. The phosphorous compound reacts with hydroperoxides by reducing them to alcohols in a non-radical process, while it oxidizes simultaneously to the corresponding five-valent derivative as shown in reaction (13).

$$(13) \qquad ROOH + P(OAr)_3 \rightarrow ROH + O{=}P(OAr)_3$$

The oxidation of both phosphates and phosphonites by hydroperoxides happens almost instantaneously. The rate at which it happens is controlled by the chemical structure of the stabilizer. The rate decreases with increasing electron-acceptor ability and bulk of the groups bound to the phosphorus atom in the order: phosphonites > alkyl phosphites > aryl phosphites > hindered aryl phosphites. When sterically hindered aryl phosphites react with oxy radicals, by substitution sterically hindered phenoxy radicals are released, therefore they can also act as antioxidants to some extent as shown in Figure 12.

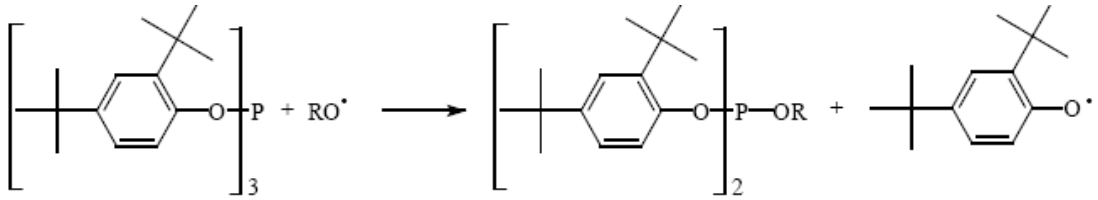


Figure 12. Phosphite antioxidants action mechanism[32]

Under processing conditions aryl phosphites show important antioxidative efficiency. For this reason phosphites and phosphonites are used as stabilizers during melt processing. As the rate constant of the reaction between peroxy radicals and hindered aryl phosphites reduces considerably at service temperatures their

contribution to the stabilization of the end product is negligible in service.

1.5.4 Organosulphur antioxidants

Organosulphur compounds such as sulfides, dialkyl dithiocarbamates or thiodi-propionates are efficient hydroperoxide decomposers[33, 34]. The sulfide function reacts stoichiometrically with a hydroperoxide molecule generating a sulfoxide. Sulfenic acid is formed through thermal decomposition of the intermediate sulfoxide[34]. Further possible reactions are the formation of sulfone or oxidation with hydroperoxides as shown in Figure 13.

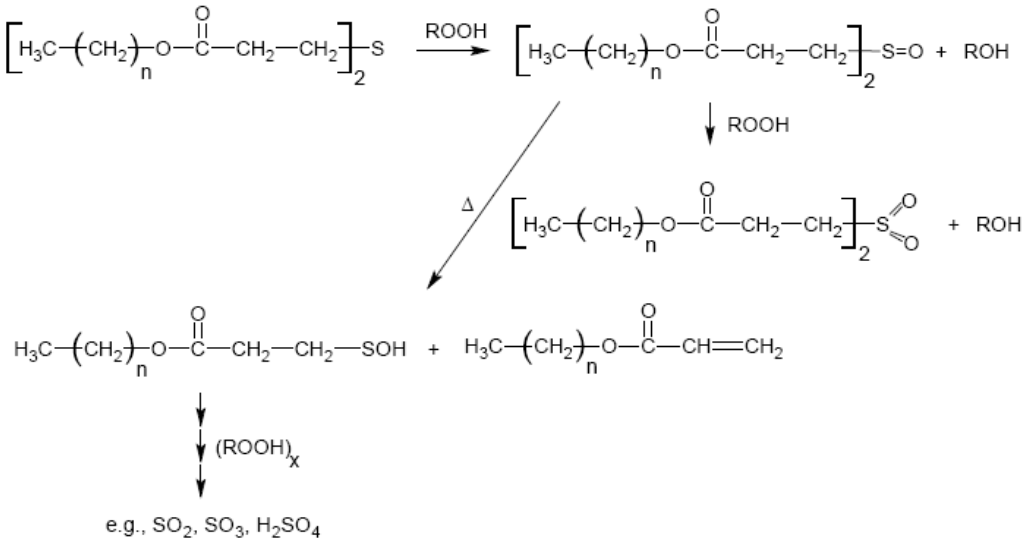


Figure 13. Organosulfur antioxidants action mechanism[32]

Natural gas and propane are colourless and odourless. To make them easy to detect in case of a leak, a small amount of methyl mercaptan CH_3SH or ethyl mercaptan C_2H_5SH is added to the gases. It is interesting to point out that these additives are sufide compounds. They could become implicated in the reaction above. Strong odours of Mercaptan were noticed while conducting test involving the melting of the pipe material. The merccaptans could have been trapped in the amorphous regions of the Aldyl A material where it is believed that it was acting as a hydroperoxide decomposer.

1.6 Polyethylene pipes in the UK gas industry

The original high-density polyethylene (HDPE) pipe materials, developed in

the mid-1950s, were difficult to joint and were less tough than the medium density polyethylene (MDPE) finally selected for potable water distribution. The test standards specified by the gas industry agreed to the use of MDPE in the late 1960s[35]. Thus in 1969, high density and medium density polyethylene material were under development for British gas. MDPE was preferred to HDPE for the transport of gas due to its superior ductility, long-term stress crack resistance and weldability[35]. Initially modern PE systems were used in the UK low pressure gas distribution (below 2 bars). In the early 1990s with the introduction of PE100 materials it was possible to use PE pipes in high pressured system[35] (up to 7 bars).

1.6.1 History

In 1969 Polyethylene (PE) gas pipes and fittings were introduced to the UK. First, imperial-sized DuPont Aldyl A PE pipes and fittings were imported from USA. 2 years later, in 1971, DuPont production started in the UK still using the imported USA Aldyl A (PE-A) polymer resin. Various grades of the Aldyl A resin were produced until 1990 [36]. Originally, imperial sizes of the Aldyl A pipes were manufactured, but the production changed to metric sizes following the implementation of the British Gas Specification PL2-1[37] in 1976. With the sale of DuPont to Uponor (Neste) in 1991, there was a further production change to use BP Rigidex 002-40 (at the time referred to as PE-X) material from Grangemouth, Scotland. Following this, similar PE-X materials were imported from Europe. The materials were mainly sourced from Borealis, Fina, Solvay and BP. They later became classified as PE80, leaving the term "PEX" for crosslinked PE materials.

From 1973 other UK based manufacturers, augmented their supply with metric pipe and fittings made of PE80 type polymer from BP and other European sources. Shortly afterwards in 1976, British Gas decided to allocate pipe supply to separate regions in order to avoid mixing imperial Aldyl A and metric PE80 material in the regional networks.

In 1969, tan-coloured Aldyl A pipes and fittings were produced from the original Alathon 5040 grade. The tan pipes were made using the masterbatch[36] process which involved the mix of natural and pigmented pellets in the pipe extruder.

In 1971, the DuPont (UK) Hilcote factory started the production of yellow

imperial-sized pipe and fittings using the Alathon 5043 resin; but some tan Alathon 5043 was also available at this time. The change in colour could indicate the modification in the additive package of antioxidants and UV stabilisers.

DuPont made a considerable alteration to its Aldyl A resin formulation in 1984[36]. The enhanced resin, known as Alathon 5046-C, was marketed as "Improved Aldyl A", and radically improved the Aldyl A pipe's performance toward its resistance to "Slow Crack Growth" by adding more co-monomer to the formula[36, 38].

In 1988, DuPont introduced the Alathon 5046-U. This change in resin formulation improved the resistance of the pipe to slow crack growth by another order of magnitude. Furthermore, because of the high "molecular efficiency" of this new resin, its density was also reduced, which allowed superior ductility in the pipe. This product was also marketed as "Improved Aldyl A"[38].

Alathon 5044/6044 may have been used[36], possibly only for fittings in the UK gas piping system. Alathon 5046-C and Alathon 5046-U might have also been introduced in the UK gas piping system.

A summary of DuPont Aldyl A pipe produced between 1966 and 1992 is presented below in Table 1. Information includes the resin formulation, year of manufacture, density, melt index, relative resistance to slow crack growth (SCG) and summary notes. The identification of most Alathon grades can be achieved by comparing the material colour, melt index and density as seen in Table 1.

Table 1. Summary table - Aldyl A pipes history[36]

Name	Resin grade	Year of manufacture (USA)	Pipe diameter	PE type	Co-monomer	Colour	Density (g/cm^3)	Melt index (g/10min)	Typical (SCG) Resistance (Plain pipe at 8 bar, 80°C)	Comment
Aldyl "A"	Alathon 5040	1966-1970	Imperial	MDPE	Butene	Tan	0.935	2	-	Original Alathon Resin.
Aldyl "A"	Alathon 5043	1970-1983	Imperial (tan and green yellow) Metric (green yellow)	MDPE	Butene	Tan then green yellow from 1971	0.939	1.2 (later 1.1)	100h	Increased density & molecular weight to increase yield strength and meet quick burst test. Pipe production started in the UK in 1971 leading to a change of pipe colour from Tan to Yellow.
Improved Aldyl "A"	Alathon 5046-C	1983-1988	-	MDPE	Octene	Green yellow	0.939	1.1	1,000h	Changed co-monomer. Substantially improved slow Crack Growth resistance.
Improved Aldyl "A"	Alathon 5046-U	1988-1992		MDPE	Octene	Green yellow	0.933	1.1	10,000h	Added more co-monomer to improved Slow Crack Growth resistance.
GPS GM5050	GPS GM5050	1973-1974	Imperial	HDPE	-	Pale yellow	0.950	-	-	-
PE80	Various	From 1973	Metric	MDPE	-	Bright yellow	0.940	-	-	-

1.6.2 Common failure modes encountered with Aldyl-A

In 1980s, DuPont informed its Aldyl A pipe customers that pre-1970 Aldyl A pipes manufacturing process was resulting in some of the pipe having a "Low Ductile Inner Wall"[38]. This property caused the inner surface of the pipe to become brittle, and allowed the formation of cracks and premature failure.

Dupont conducted newly developed testing methods at elevated temperature which would permit a more accurate estimation of the longevity of Aldyl A pipes. Dupont reached the conclusion that the pipes manufactured prior to 1973 would not reach their minimum service life requirement of 50 years due to "rock impingement" and squeeze-off practices[38]. "Rock impingement" is created by pressure coming from rocks on the pipe exterior wall. "Squeeze-off" refers to the action of mechanically pressing in the polyethylene pipe walls to temporarily stop the flow of gas during work on a line. DuPont also noted that the average ground temperature in the area where a pipe is in service could affect its lifetime and considerably reduce it, especially for temperatures above 15 degrees Celsius [34].

The Dupont explanation for premature failures of pipes in the gas industry is widely discussed in the UK. The UK gas industry never saw clear evidence of this behaviour, but it is fair to say that the field conditions are different in the UK compared to the USA regions where brittle failure happened. Because LDIW is related to the high crystallinity of the inner pipe wall we might be able to study it through analytical techniques such as the differential scanning calorimetry.

1.6.2.1 Low ductility inner wall

Low ductility inner wall (LDIW) pipes were potentially brought in UK from the USA from 1969 until the production started in the UK in 1971[38]. LDIW is caused by degradation of the pipe bore extrusion which resulted in large coarse spherulites[38]. LDIW caused the inner surface of the Aldyl A pipe to become brittle, promoting the formation of cracks and premature failure[38].

In early 1972, DuPont changed its manufacturing process to eliminate this phenomenon, but estimated that 30 to 40% of the pipe it produced in 1970, 1971 and early 1972 was affected[38]. The exact dates of the change-over are important to determine the

likelihood of LDIW pipe installed in the UK. The fact that there has never been any reference of LDIW in the UK does not necessarily means that there are none present in the field. These pipes would be the most vulnerable to in-service failure, therefore it is important to assess the crytallinity of early tan Aldyl A grade to verify the Dupont theory and possibly remove these pipes from service if their quality is poor.

1.6.2.2 Rock contact and squeeze-off

Rock impingement[38] or "squeeze-off" are external stresses that can cause the Aldyl A pipe material to fail. The failure would starts with a crack initiation on the inside surface of the pipe wall that results in slow crack growth. The crack will propagate toward the external wall of the pipe, and finally, through-wall failure will occur. These failures appear as short, tight cracks in the outer wall of the pipe.

1.7 Lifetime determination methods

Previous studies have been carried out to determine the residual lifetime of PE material[1,39,40]. The rate process method is the most widely used process but the fracture mechanic method is also used. The antioxidant depletion method represents a new alternative to the first two and will be explained later.

1.7.1 Rate process method

A suggested way of determining residual lifetime of an old PE pipe is the Rate Process Method[39] (RPM). RPM replicates stress cracking situations in the field such as rock impingement, deflection, bending and squeeze-off. It involves exhuming pipe samples from service and subjecting them to laboratory elevated temperature, sustained pressure testing of pipe that result in slit or brittle-type failures as would be observed in the field[39].

The RPM uses a three-coefficient equation that relates time, temperature and pressure (or hoop stress). It is based on two scientific principles[39]:

- There is a linear relationship between the log of stress and the log of time.
- There is a linear relationship between the log of time and the inverse of temperature (absolute temperature in degrees Kelvin). This is the principle of Arrhenius.

By combining these two relationships, the RPM three-coefficient equation results:

(14) $$\log(time) = A + \frac{B}{T} + \frac{C\log(P)}{T}$$

Where:

Time = failure time (hours)

T = temperature (K)

P = internal pressure (psig) or internal hoop stress (psi)

A, B, C = three coefficients

RPM provides the best probability for extrapolation of data based on the statistical "lack of fit" test. As a result, the RPM has been in use for roughly 20 years. The Rate Process Method (RPM), which was developed, was included in two ASTM standards. ASTM D 2837 added a "validation" requirement for PE piping materials, and ASTM D 2513 added a validation requirement for the pipe producer.

1.7.2 Fracture mechanics method

An alternative to RPM would be to perform fracture mechanics tests[40] in order to evaluate the resistance to crack initiation and SCG. Based on a Frank extrapolation route and using cyclic fatigue tests, a fracture mechanics prediction of the remaining lifetime can be made.

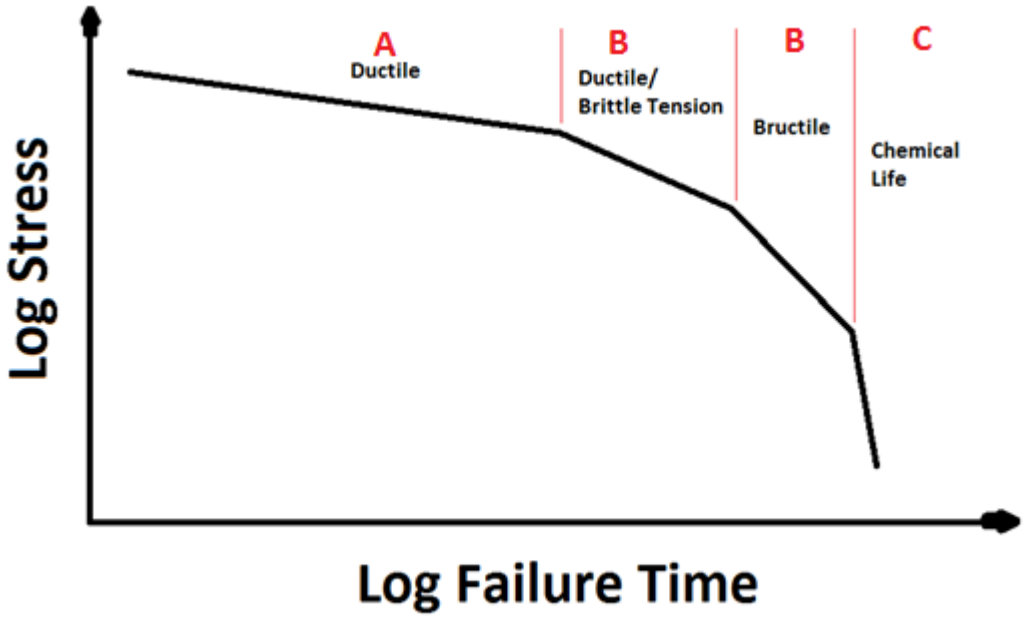


Figure 14. Schematic illustration of the failure behaviour of pressurized PE pipes[1]

Three distinctive regions characterize the failure mechanisms of internally pressurized pipes. They depend on the load level as it is schematically shown in Figure 14. The failure mechanism in region A happens within a relatively short period and appears at a relatively high stress[41]. It is essentially a ductile failure created by a large scale plastic deformation. Usually, plastics pipe systems are not designed to operate under high stress, which means that this type of failure is unlikely in service.

The failure happening in region B is more to be expected in the field[41]. With a decreasing stress, a transition knee into the quasi-brittle region B is passed and the failure is characterized by creep crack growth initiation and only small scale crack tip plasticity. It is generally accepted that this failure region determines the lifetime of long-term applications. The brittle failure region C is a result of large scale material ageing and polymer degradation and is nearly load-independent[41].

Frank[40] developed a method for the lifetime determination of pipe that already had a growing crack. This was done using fatigue tests with circumferentially cracked round bar (CRB) which were put under different loading ratios.

The following equation resulted:

(15) $$t_{CCG} = \frac{1}{A} \cdot \int_{a_{ini}}^{a_f} \frac{1}{K_I^m} \cdot da$$

$$t_f = t_{tot} \sim t_{in} + t_{CCG}$$

Where

t_{CCG} is the time for creep crack growth from an initial starter defect

K_I is a stress intensity factor

a_{ini} is the initial starter defect

a_f is the final defect size

A and m are parameters depending on the material, the temperature and the loading conditions.

This method permitted an assessment of the quality of pipes in the event of crack propagation and eventually a "lifetime prediction".

1.7.3 Antioxidant depletion

There was an attempt at residual lifetime determination of PE pipe in 2009 by E. Hoang and D. Lowe[1]. This approach was based on antioxidant consumption and initiation of thermo-oxidative degradation in the PE100 water pipe grade material. The leachage of antioxidants due to water exposure and the oxidative reaction to protect the pipe against thermal oxidation was monitored by the oxidative induction time (OIT) testing. Furthermore, the initiation of thermo-oxidative degradation was measured by iodometric detection of hydroperoxides. The Arrhenius fit of the data was developed to extrapolate the lifetime of the PE100 pipe material at diverse service temperatures.

$$\ln S_T = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln C$$

Where S_T is the reaction rate (rate of depletion of antioxidants) at test temperature T(K), Ea is the activation energy of the reaction (depletion of antioxidants) (kJ/mol), R is the gas constant (8.31 $J.K^{-1}.mol^{-1}$), C is a constant independent of test temperature T. This method combining pressure testing and chemical analyses was proved to be a powerful tool to extrapolate the lifetime of plastic pipes.

1.8 Method for the lifetime determination

The Antioxidant depletion technique was chosen over the RPM and the fracture mechanics method for the lifetime determination of the Aldyl A material. Once the lifetime determination formula is found the technique will offer the following advantages:

- This method can be integrated easily in the working/intervention plans of the operators: a simple shaving of the outside surface of the pipe is required to conduct the testing and find out the residual lifetime of the material analysed.
- The procedure requires only very small quantities of material of the order of 5mg for the best consistency of the results.
- The test is fast, accurate and easy to interpret.
- The same lifetime determination formula can be used for identical material.

This method is only worth trying if the material can easily be identified. MFR and density can be used to identify some of the PE type and material grades but only to an extent. The SIS technique can be a great alternative to these methods.

In the 1990s, the SIS technique was developed to provide an accurate characterisation of the more and more complex PE resins manufactured and commercialised for the market[42]. In 1995, Gueugnot and al. published a modified version of the SIS protocol[43, 44,45,46] which got rid of anomalies happening for medium density PE pipes displaying premature failures through hydrostatic pressure testing. The SIS technique is relatively new and is still in process of being developed. Some researchers have tempted to couple this technique with other complementary analytical tools such as TREF used for polymer fractionation[47]. The SIS protocol consists of a sequenced heating-cooling treatment of the plastic material in order to distinguish macromolecular species with respect to their respective crystallizabilities. For this purpose the DSC instrument is used.

Hence DSC-SIS technique is a powerful and accurate tool to identify PE resins. The technique allows a rapid characterisation of the field specimen by comparing its fingerprint to reference PE in a database. The technique only requires a small amount of material (around

30 mg or less), therefore pipe scrapping may be tested directly.

If the residual lifetime determination is possible through the antioxidant depletion method, only the DSC instrument will be required for the whole process. This involves identifying the material using the SIS technique and determining its remaining lifetime using the OIT technique. Furthermore, none of the techniques require large amount of material, they can both be executed on pipe shavings.

2 Chapter II: Experimental

2.1 Material identification

Pipes were exhumed from various locations in the UK, the differences noticed in the pipes colours were noted. The pipes diameters were recorded as the change from imperial to metric dimensions could help with their identification. Not all the pipes could be supplied in enough quantity to allow the work on the residual lifetime determination to take place. However, as all the analytical techniques employed for the identification did not require vast amount of material, the identification work was conducted for a large proportion of the pipes exhumed. A list of the exhumed pipes containing the pipes colour, diameter and year of manufacture can be consulted in Table 2. Due to a confidentiality agreement it was not possible to display the pipes location in the table however it was possible to define the area corresponding to the city and the city surroundings to which the pipe was taken from. The year of manufacture was taken from the pipe directly.

Table 2. List of exhumed pipes[48]

Sample	Pipe/Fitting detail	Date manufacture	Colour	Area number	Material
3205-1 A	?	?	green yellow	N/A	N/A
3205-1 B	?	?	green yellow	N/A	N/A
3205-2	?	?	green yellow	N/A	N/A
3205-3	?	?	discoloured to black	N/A	Muntz Barwell
3205-4	3"	1974	green yellow	1	Aldyl A
3205-6B	3" SDR 11	1978	green yellow	2	Aldyl A
3205-7	4" SDR 11	1981	green yellow	1	Aldyl A
3205-9A	2" SDR 11	1975/1976	green yellow	1	Aldyl A
3205-11	90 mm SDR 11	1985	green yellow	N/A	Aldyl A
3205-12	63 mm SDR 11	1987	green yellow	N/A	Aldyl A
3205-13	2" SDR 11	1977	green yellow	N/A	Aldyl A
3205-19	63 mm SDR 11	1980	green yellow	N/A	Aldyl A
3205-21A	4" SDR 11	1979	green yellow	N/A	Aldyl A
3205-24A	2"	1971	tan	5	Aldyl A
3205-32A	3"	1972	green yellow	Other	Aldyl A
3205-34A	2"	1979	green yellow	3	Aldyl A
3205-35	2"	1974	green yellow	3	Aldyl A
3205-36-1 A	6"	1978	green yellow	4	Aldyl A
3205-37 F	6"	1977	green yellow	4	Aldyl A
3205-38 A	8"	1981	green yellow	Other	Aldyl A
3205-39 C	3"	1978	green yellow	2	Aldyl A
3204-41	4"	1975	green yellow	2	Aldyl A
3025-42 A	4"	?	green yellow	2	Aldyl A
3205-43 A	4"	1976	green yellow	2	Aldyl A
3205-44 A	4"	1975	green yellow	2	Aldyl A
3205-45 A	6"	1978	green yellow	3	Aldyl A
3205-45 D	6"	1978	green yellow	3	Aldyl A
3205-49 A	4"	1985	tan	USA	Aldyl A
3205-50	4"	1986	tan	USA	Aldyl A
3205-51	4"	1986	tan	USA	Aldyl A
3205-52 A	2"	1990	tan	USA	Aldyl A
3205-53 A	180mm	1987	green yellow	N/A	Aldyl A
3205-57 A	2" SDR 11	1976	green yellow	8	Aldyl A
3205-58	2" SDR 11	1974	pale yellow	Other	HDPE
3205-59 A	4" SDR 11	1978	green yellow	2	Aldyl A
3205-64 G	4" SDR 11	1977	green yellow	2	Aldyl A
3205-65 A	125mm SDR 11	1972	bright yellow	7	Other MDPE
3205-66 A	2" SDR 11	1979	green yellow	5	Aldyl A
3205-67 A	3" SDR 11	1977	green yellow	5	Aldyl A
3205-68 A	2" SDR 11	1971	tan	6	Aldyl A

Sample	Pipe/Fitting detail	Date manufacture	Colour	Area number	Material
3205-68 E	2" SDR 11	1971	tan	6	Aldyl A
3205-78 A	3"	1976	green yellow	4	Aldyl A
3205-81 A	1"	?	green yellow	2	Aldyl A
3205-83 A	2"	1981	green yellow	N/A	Aldyl A
3205-84 A	2"	1981	green yellow	N/A	Aldyl A
3205-85 A	2"	1981	green yellow	N/A	Aldyl A
3205-86 A	2"	1981	green yellow	N/A	Aldyl A
3205-88 A	4"	?	green yellow	7	Aldyl A
3205-90 A	2"	1975	green yellow	7	Aldyl A
3205-92 A	4"	1974	green yellow	7	Aldyl A
3205-94 A	125mm 90° EF elbow joint	?	green yellow	7	N/A
3205-94 C	125mm	?	bright yellow	7	N/A
3205-95 A	2"	1974	pale yellow	Other	N/A
3205-103 B	6"	1988	green yellow	4	Aldyl A
3205-106 A	2"	1975	green yellow	4	Aldyl A
3205-109 C	1"	?	green yellow	8	N/A
3205-109 D	1"	?	bright yellow	8	N/A
3205-110 A	1"	1979	green yellow	8	Aldyl A
3205-115 A	2"	1976	green yellow	Other	Aldyl A
3205-116 A	3"	1977	green yellow	Other	Aldyl A
3205-117 A	4"	1970	tan	4	Aldyl A
3205-118 A	3"	1972	green yellow	8	Aldyl A
3205-118 D	2"	1978	green yellow	8	Aldyl A
3205-119 A	8"	1979	green yellow	7	Aldyl A
3205-122	180 mm	1978	bright yellow	7	N/A
3205-123	315 mm	?	green yellow	7	N/A
3205-126 A	125 mm SDR 11	1978	bright yellow	7	Other MDPE
3205-127 A	125 mm	?	bright yellow	7	Other MDPE
3205-127 B	125 mm HI tee	?	bright yellow	7	Other MDPE
3205-133 A	90 mm	1982	green yellow	Other	Aldyl A
3205-139 A	1/2"	?	bright yellow	1	N/A
3205-139 B	1/2"	?	bright yellow	1	N/A
3205-139 C	1/2"	?	bright yellow	1	N/A
3205-139 D	1/2"	?	bright yellow	1	N/A
3205-139 E	3/4"	?		1	N/A
3205-141 A	2" SDR 11	?	bright yellow	8	HDPE
3205-141 C	2" SDR 11	?	bright yellow	8	HDPE
3205-141 D	1" SDR 11	?	bright yellow	8	HDPE
3205-141 E	2" SDR 11	?	pale yellow	8	HDPE
3205-147	2" SDR 11	1973	green yellow	6	Aldyl A
3205-148 A	4 1/2"	?	green yellow	N/A	N/A

Sample	Pipe/Fitting detail	Date manufacture	Colour	Area number	Material
3205-150-1	6"	?	green yellow	Other	N/A
3205-163 A	8" SDR 21	1975	green yellow	1	N/A
3205-165 A	3" SDR 11	1970	tan	4	Aldyl A
3205-168 B	4" SDR 11	1975	green yellow	4	Aldyl A
3205-169 B	6"-1" HI top tee	1975	tan (pipe 169 A is green yellow)	4	Aldyl A
3205-177	4" SDR 11	1979	green yellow	2	Aldyl A
3205-178 J	6" SDR 17	1974	green yellow	2	Aldyl A
3205-184 D	2"-2" HI tee	?	tan	2	N/A
3205-187	3" SDR 11	1970	tan	4	Aldyl A
3205-188	1" SDR 11	1971	tan	4	N/A
6803 (PE80)	180 mm SDR 11	2012	bright yellow	N/A	PE80
6804 (PE100)	125 mm SDR 11	2012	black	N/A	PE100

A SDR 11 means that the outside diameter of the pipe is eleven times the thickness of the wall.

In order to identify the different grades of Aldyl A material as well as the HDPE material, melt flow rate (MFR), density tests and a relatively new technique called Stepwise Isothermal Segregation (SIS) involving the differential scanning calorimetric instrument (DSC) were performed.

2.1.1 Melt flow index measurement

The melt flow rate (MFR), is determined by the weight of polyethylene extruded over 10 minutes at 190 °C through a standard die and using a piston load of 2.16 kg. Reported in g/10min, the melt index is measured using an instrument called extrusion plastometer according to EN ISO 1133[49] condition 190/2.16.

Pipes exhumed from the field were cut into pellets for MFR testing using the band saw. The pipes melt-flow rates were obtained according to EN ISO 1133[50], using a CEAST MFT, Type 6934.00 melt-flow indexer. A small quantity of the pelletized sample to be tested was fed into the hot barrel. The loaded piston was applied for 60 seconds then the load was removed to allow the sample to heat for 5 minutes. After this time, the full 2.16 kg mass was reapplied and cut-offs were taken at suitable regular intervals automatically. The melt flow rate (MFR) was calculated using the theoretical density of the polymer (0.7636 g/cm^3 for PE) and was quoted as the

number of grams of material extruded in 10 minutes.

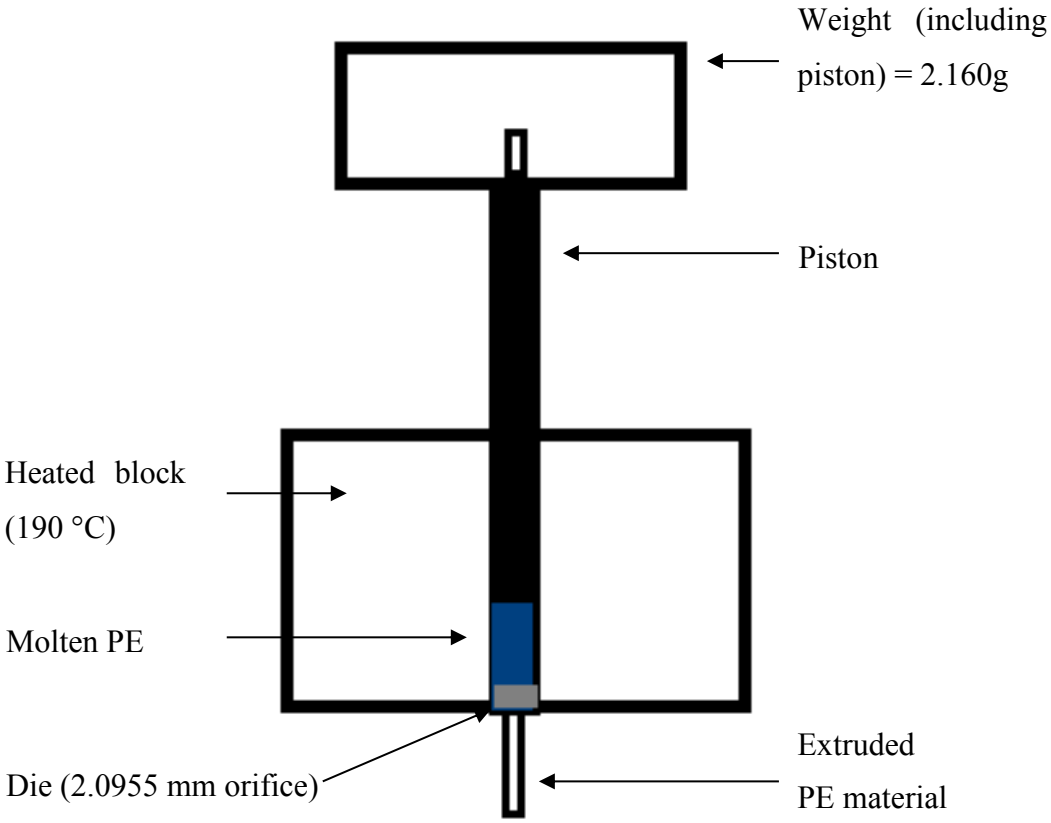


Figure 15. Schematic of the MFR instrument

2.1.2 Density measurement

The melt processing to which the pipes were subjected when being manufactured in the late 1960s did not allow a constant density through the pipe wall. The density is known to change between the internal and external surfaces as a result of the greater cooling rate experienced during manufacture at the outside surface. It is therefore necessary to erase the processing history of this material in order to prevent the variation in density depending on the sample location before conducting the test. This was carried out by cutting a small section of the pipes into 2x2 mm pellets. To erase the processing history the pellets were melted in the hot MFR barrel. The samples were not left more than 25 min inside the barrel as per the EN ISO 1133.

A small, through thickness, sample was cut from the MFR extrudate of the MFR test. Each slice was cut to a different shape to aid recognition in the density column. Thickness was measured with a calibrated micrometer accurate to +/-0.05 mm prior to immersion. The length of the shape of the sample should be less than 5

mm according to EN ISO 1183[51]. Densities were measured in a density column gradient made out of an isopropanol/water solution. The density range covered was varying from 0.9098 to 0.9871 g/cm^3.

2.1.3 Stepwise isothermal segregation

The SIS method is a PE crystal lamellar thickness driven segregation technique using DSC for a sequenced heating-cooling-heating treatment of the material. The SIS technique is used to characterise short chain branching distributions via their effect on lamellar thickness distribution.

SIS measurements were conducted using a Perkin–Elmer DSC 4000 differential scanning calorimeter. The sample mass was in the range of 14.5 mg to 15.5 mg. The temperature and enthalpy scales of the instrument were calibrated using indium and tin standards. The Aldyl A samples were placed in aluminium pans and covered with aluminium lids. The stepwise isothermal segregation process [52, 53] involves the polyethylene samples first being heated to 170 °C at 10 °C/min under a dry nitrogen atmosphere and held at this temperature for 1 minute. Then the sample is crystallised in steps at preset temperatures. The crystallisation temperatures chosen were 124, 119 and 114 °C. The first two temperatures were held for 30 minute while the last temperature was held for 15 minute. If larger temperature steps were taken, the polymer would take longer to equilibrate at each temperature because equilibration is a logarithmic process[54]. After complete crystallization, the samples are cooled to 25 °C at 20 °C/min, and the heating curve from 25 to 170°C at 2.5 °C/min is recorded. Melting temperatures and degree of crystallinity were determined from the melting endotherms obtained for a rate 2.5 °C/min. The temperature programme is summarised in Figure 16.

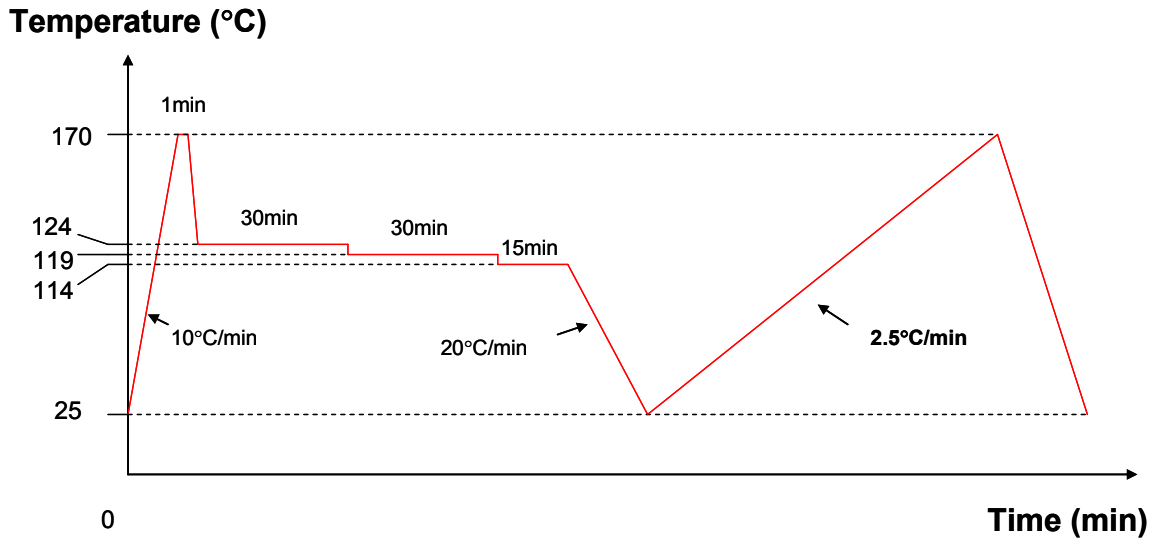


Figure 16. SIS method

2.2 Monitoring of Polyethylene Degradation

In this project, old PE pipes will be thermo-aged in water in order to accelerate their degradation. Before starting the ageing work, it is important to access their quality in terms of degradation. The old PE pipes are not expected to have reached stage C of their life where polymer degradation is predominant[41], as seen in Figure 14. If it was the case the gas network would be experiencing brittle failures on a large scale[41].

Polymer degradation starts when there is no antioxidant left in the material. Polymer degradation can be detected via infrared spectroscopy, but also using the oxidation induction time technique. On the infrared spectra, signs of degradation would be carbonyl peaks. On the OIT thermograms, polymer degradation would show by revealing OIT values close or equal to zero minute.

2.2.1 Infrared spectroscopy

Spectroscopy techniques are widely used by chemists to identify completely unknown polymers and may be used to determine the presence of specific functional groups or even free radicals and polymer additive [55]. Interpretation of the spectroscopic data in practice can be done by comparing the spectra of the outside and bore surfaces of a pipe with its middle unaltered surface. Infrared spectroscopy (FTIR) was carried out directly on the bore, middle and outside surfaces of the PE material using an ATR (attenuated total reflectance) sampling accessory fitted with a diamond/ZnSe crystal. The infrared fingerprint was reported over the spectral range 4000-600 cm^{-1} at a resolution of 4 cm^{-1}. Each pipe was tested on the bore, middle and outside surface of the serviced pipe material. One replicate spectra was collected for each pipe surface. Repeats were only conducted when sign of degradation was detected.

2.2.2 Oxidation induction time

Oxidation induction time (OIT) analysis is a standardized test performed in a DSC that measures the level of stabilization of the material tested. The time between melting and the onset of decomposition in isothermal conditions is measured.

Oxidation induction time (OIT) analysis was carried out using a Perkin Elmer DSC 4000 in general accordance with ISO/TR 10837[56]. The temperature and enthalpy scales of the instrument were calibrated by using indium and tin standards.

The method involved an initial starting temperature at 25°C, increasing to 200°C at 20°C/min under a 50 ml/min nitrogen gas flow. After a 5 min holding period at 200°C the gas was switched from nitrogen to oxygen at 50 ml/min and the temperature was kept to 200°C until the end of the oxidation. The temperature programme is summarised in Figure 17.

Disc specimens were cut from the bore, middle and outside part of the old pipe material. Sample masses of 5 ± 0.5 mg were tested. OIT data were measured in minutes and were used to assess polymer degradation stages.

The first stage of the OIT (from the start of the test to the beginning of the isothermal step) was used as it was indicative of the melting of the material. However the T_m values did not allow differentiation between material grades and SIS, which provide information on short chain branching is expected to be a better technique. Therefore the melting peak was not recorded.

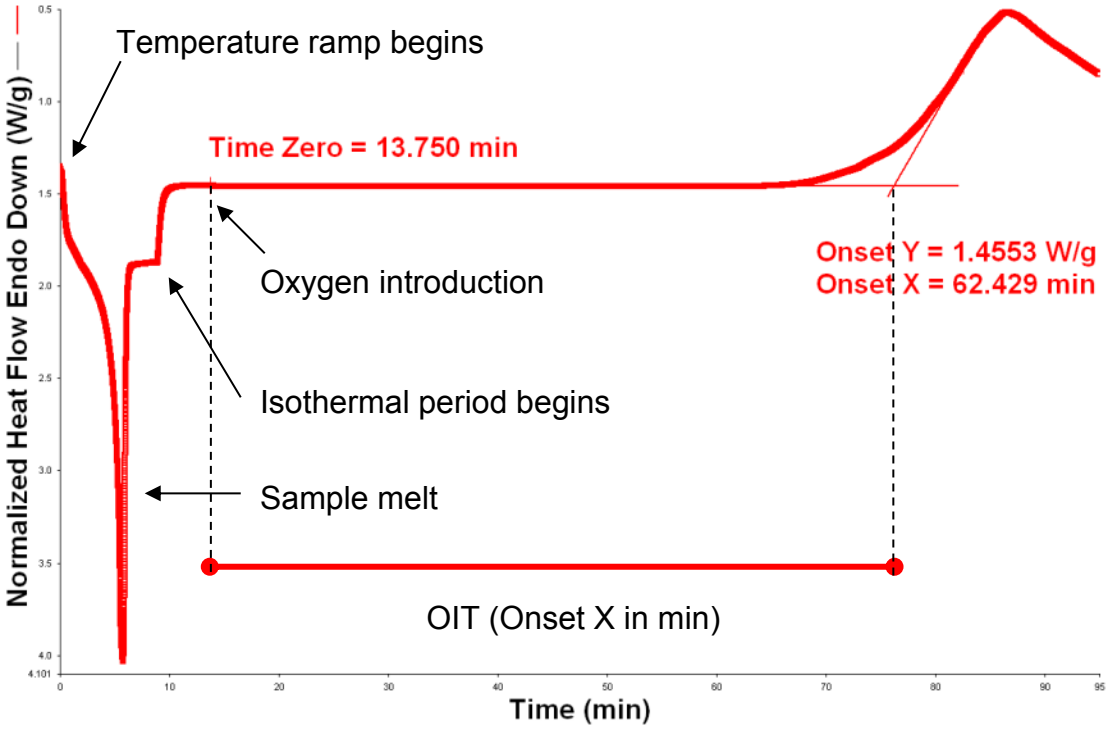


Figure 17. Schematic of the OIT thermogram

Each serviced pipe was tested for OIT once at the bore, middle and outside

surfaces. OIT was repeated to check for variation in the chemical composition for some pipe grade materials.

2.2.3 Thermogravimetric analysis

2.2.3.1 Thermogravimetric analysis – heating scan

Thermogravimetric analysis (TGA) is a common method to study the kinetics of polymer degradation. TGA measures the amount and rate of change in the weight of a material against temperature or time in a controlled atmosphere. Measurements are used mainly to establish the composition of materials and to predict their thermal stability at temperatures reaching up to 1000°C. Weight loss or gain due to decomposition, oxidation, or dehydration can easily be studied using this technique. TGA was used as an attempt to find a correlation between thermogravimetric loss and different grades of Aldyl A.

TGA measurements were performed using a Perkin Elmer TGA 4000 calibrated in accordance with the manufacturer's recommendations. Samples with a mass varying between 10.0 and 10.5 mg were placed in a 180 µL AlO_x crucible and heated from 25 to 900°C at 10°C/min under 50 ml/min of oxygen gas flow. Serviced pipes were tested by TGA once at the middle surface.

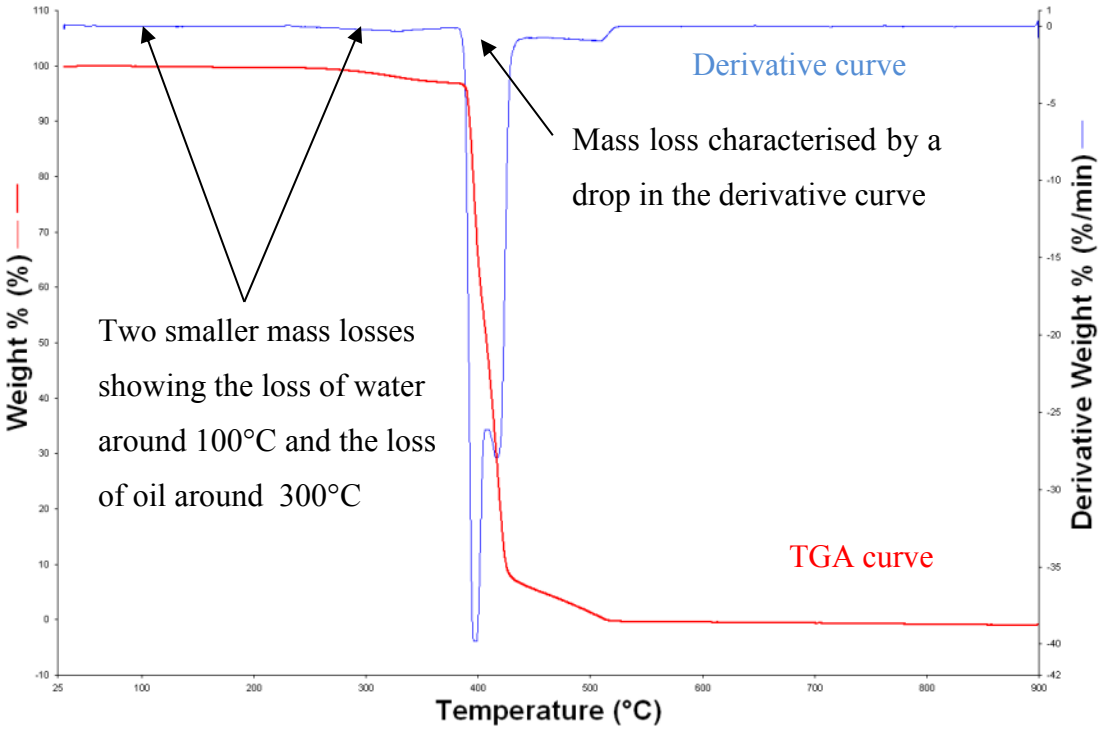


Figure 18. TGA thermogram of a PE material (N_2 flow (50 ml/min) up to 600°C then switching to O_2 flow (50 ml/min) with a heating rate of 10 °C/min)

2.2.3.2 Thermogravimetric Analysis – isothermal scan

TGA was also conducted in isothermal mode in a similar manner to the OIT determination (according to the ISO/TR 10837). The method involved an initial starting temperature at 25°C, increasing to 200°C at 20°C/min under a 50 ml/min nitrogen gas flow. After a 5 minute holding period at 200°C the gas was switched from nitrogen to oxygen at 50 ml/min and the temperature was kept to 200°C until degradation occurred.

Disc specimens were cut from the bore, middle and outside part of the pipe material. Sample masses of 5 ± 0.5 mg were tested. TGA data was measured in minutes and compared to the results obtained using the DSC instrument.

2.3 Hydro-Thermal Ageing

2.3.1 Pipe selection

The pipes were selected from the list of samples given in Table 2. First the

pipes were identified and then a selection of 10 pipes was defined. The pipes were selected on the basis of their availability for testing, meaning that they were only chosen if there was sufficient material available to also perform eventual mechanical testing. The mechanical testing conducted on the pipes is not discussed in this report but was part of a larger on-going project.

2.3.2 Preparation of samples for ageing

In service, the environment on the inside of the pipe material is a mix of methane and mercaptan. The outside environment is air/water/backfill. The internal environment was thought to be benign in terms of degradation of the pipe material. The external environment was thought to be aggressive as the abundance of oxygen outside of the pipe in service could contribute to deterioration of the pipe material. This situation (benign on the bore part and aggressive on the outside part of the pipe) could be simulated by masking the bore and edge surfaces using a suitable surface coating.

The samples inside and side surfaces were then coated in high temperature resistant silicone. The red silicone sealant Geocel Trade Mate Plumba Flue was chosen for the protection of the bore part of the pipe against the hot water. This silicone could resist temperatures going up to 300°C. To avoid leaving the samples out of the water environment for too long when collecting samples for the OIT testing, half pipes sections of 25 cm length were cut into 2 x 2 cm sized blocks.

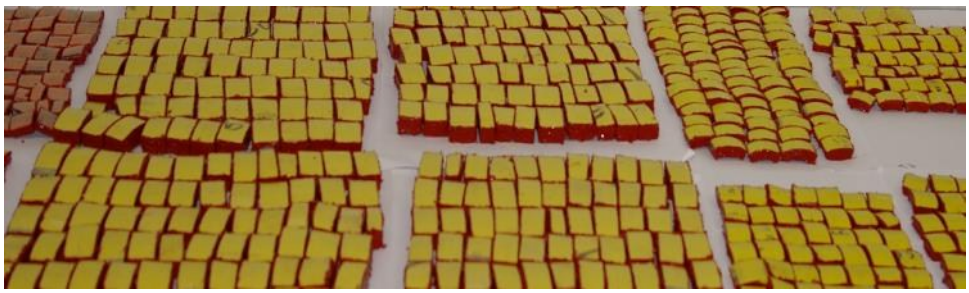


Figure 19. One side silicone coated samples

The test pieces were enclosed within stainless steel mesh bags. At first, the sample blocks were organised to allow the hot water to have an even access to the external surface of the blocks. Unfortunately, the samples were brought back to an unorganised arrangement each time that the mesh bag was opened for sample collection. As the water was circulating freely in the bags and because the samples did

not form clusters or stick to each other, it is not believed that the arrangement of the samples in the bag had an impact on the OIT results.

Figure 20. Sample held in mesh bags

The bag containing the samples were labelled and then placed in temperature controlled baths. Bath temperatures were set at 60, 70, 80 and 90°C. It is appreciated that 90°C is close to the T_m of MDPE and HDPE (between 120-130°C), it was nevertheless decided to work at this temperature as it would provide the maximum acceleration of ageing whilst the pipe is in the solid state. Tap water was used as the heat transfer medium. An additional calibrated temperature recording device was used to verify the test temperatures.

Evaporation of the water was reduced via use of a polyethylene sheet on top of a layer of floating hollow polypropylene balls on the surface of the hot water. When topping up of a bath was necessary, hot water was used in order to reduce equilibration time.

During sample collection for OIT testing the samples were not kept out of the bath more than 5 min.

2.3.3 Oxidation induction time testing

Samples were regularly removed from the bath and subjected to OIT determination. The OIT would be recorded as a function of immersion time for a specified temperature.

3 Chapter III: Results and discussion

3.1 Material identification

3.1.1 Melt flow rate and density measurements

As soon as a pipe was exhumed, its colour was noted (Figure 21). The samples were classified in Table 2. A large proportion of the pipes exhumed will be discussed.

Figure 21. Examples showing variation in pipe colour; from left to right, green yellow, bright yellow, pale yellow and tan pipe colour

MFR measurements are inexpensive, relatively easy to conduct and are indicative of molecular weight and molecular weight distribution. Molecular weight affects the melt viscosity of a polymer. Melt flow rate is inversely related to molecular weight. Therefore, resins that have a low molecular weight flow easily and thus, have a high melt flow rate. Longer chain length resins in the other hand resist flow and have a low melt flow rate. Actual molecular weights may be found using a diversity of analytical methods, including gel permeation chromatography (GPC) and viscometry. However, these methods are more costly and difficult to carry out and they do not lend themselves to routine quality control procedures.

Tan coloured pipes were introduced to the UK from the USA until 1971 when the UK

started its own production. The resin produced then was called as Alathon 5040. In 1970 DuPont changed the resin to improve the resistance of Aldyl A to rupture during pressure testing with a new resin named as Alathon 5043. When production stated in the UK in 1971 the pipe colour was also changed from tan to yellow. Some of the tan coloured pipes exhumed could be either Alathon 5040 or 5043 grade. An easy way to find out would be to conduct MFR tests. The Alathon 5040 and the Alathon 5043 have MFR values of 2 g/10min and 1.2 g/10min respectively. The melt index for the Alathon 5043 grade changed later to 1.1 g/10min.

When possible, pellets of full pipes sections (bore, middle and outside) were analysed using the BS1133 condition 190/2.16. Because of the instrument limitation, MFR with values lower than 0.06 g/10min could not be analysed using a 2.16 kg load, but results were found using a higher load of 10 kg.

3.1.1.1 *Identification of tan pipe sample*

Table 3 shows the grade classification for the tan coloured MDPE pipes from MFR and density results. Melt indexes for Alathon 5040 grades vary from 1.90 to 2.41 g/10min. Melt indexes for Alathon 5043 grades vary from 0.98 to 1.36 g/10min. After 40 years in service it is expected that thermo-oxidative degradation of the material would have occurred and the MFR values would thus be affected. Degradation has a profound effect on thermoplastic properties because they are directly linked to the molecular weight distribution (MWD). Polymer chains can be susceptible to breakage by a variety of mechanisms. Oxidised broken chains fragments may remain active long enough to take place in further reactions. Their activity can be terminated internally leading to a shorter version of the original chain but with a different end grouping. Chain extension and branching are both possible. It assumed that after 40 years in service degradation resulting in chain scission as well as chain branching would have taken place within the Aldyl A pipes.

Table 3. Identification of the tan PE pipes

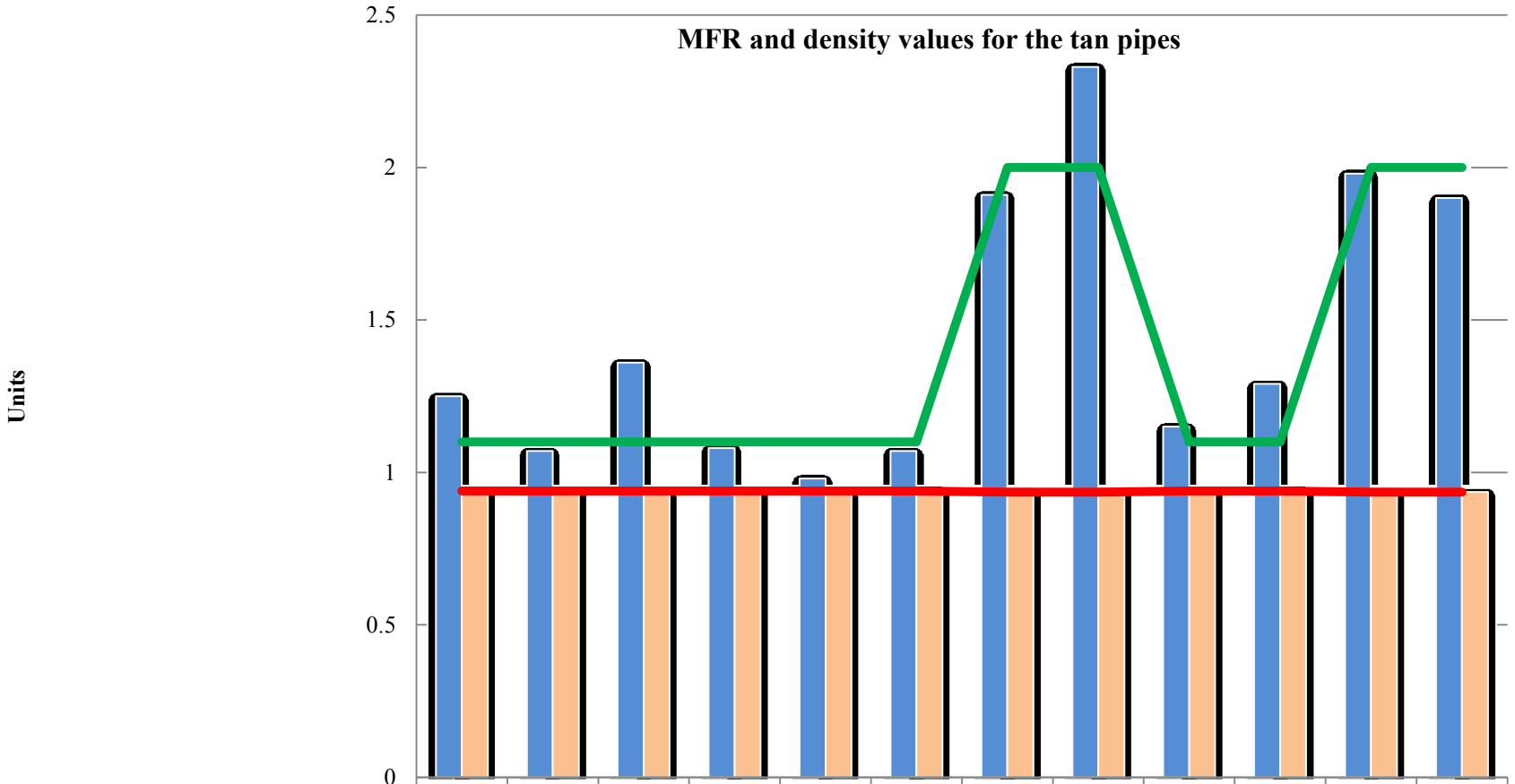
Exova Code	Colour	MFR 2.16 kg (g/10min)	Density (g/cm^3)	Identification
3205 024A	Tan	1.25	0.941	Alathon 5043
3205 049A	Tan	1.07	0.941	Alathon 5043
3205 050	tan	1.36	0.933	Alathon 5043
3205 051	tan	1.08	0.941	Alathon 5043
3205 052A	tan	0.98	0.934	Alathon 5043
3205 068E	tan	1.07	0.942	Alathon 5043
3205 117A	tan	1.91	0.938	Alathon 5040
3205 165A	tan	2.33	0.939	Alathon 5040
3205 169B	tan	1.15	0.941	Alathon 5043
3205 184D	tan	1.29	0.942	Alathon 5043
3205 187	tan	1.98	0.938	Alathon 5040
3205 188	tan	1.90	0.936	Alathon 5040

A decrease in MFR value would be indicative of a cross-linking dominated mechanistic pathway while an increase in MFR would indicate that chain scission dominated degradation has taken place.

It would be interesting to compare the SIS thermograms of the Alathon 5040 grade pipe to determine if chain scission or crosslinking have affected the results. Cross-linking may lead to a reduction in crystalline content and it is difficult to explain how this will affect the SIS results. Crosslinking is likely to happen in the less branched sections of the chains which form the thicker lamellae. Chain scission will be dominant in the highly branched sections of the polymer which constitute the thinner lamellae.

It would also be interesting to compare all the SIS thermograms of the Alathon 5043 and look for similarities. The change of melt index from 1.2 to 1.1 g/10min could have been a result of the introduction of more long chains in the resin. The SIS will not be able to compare molar masses.

In Figure 22, the density and MFR values acquired in the laboratory are compared with the expected MFR and density values for the tan PE pipes.



	3205 024A	3205 049A	3205 050	3205 051	3205 052A	3205 068E	3205 117A	3205 165A	3205 169B	3205 184D	3205 187	3205 188
MFR 2.16 kg (g/10min)	1.25	1.07	1.36	1.08	0.98	1.07	1.91	2.33	1.15	1.29	1.98	1.9
Density (g/cm3)	0.941	0.941	0.933	0.941	0.934	0.942	0.938	0.939	0.941	0.942	0.938	0.936
Expected MFR 2.16 kg (g/10min)	1.10	1.10	1.10	1.10	1.10	1.10	2.00	2.00	1.10	1.10	2.00	2.00
Expected density (g/cm3)	0.939	0.939	0.939	0.939	0.939	0.939	0.935	0.935	0.939	0.939	0.935	0.935

Figure 22. MFR and density values for the tan pipes

3.1.1.2 Identification of bright yellow pipe samples

The MFR results for the bright yellow pipes were similar to the MFR result of the modern PE80 material. These materials are thought to be made of the same MDPE material (MDPE 1).

In Table 4, some of the pipes could not be classified as MDPE 1 with a high degree of certainty because their MFR could not be found using the 2.16 kg standard load. The material was so viscous that a 10 kg load had to be used for the MFR measurement.

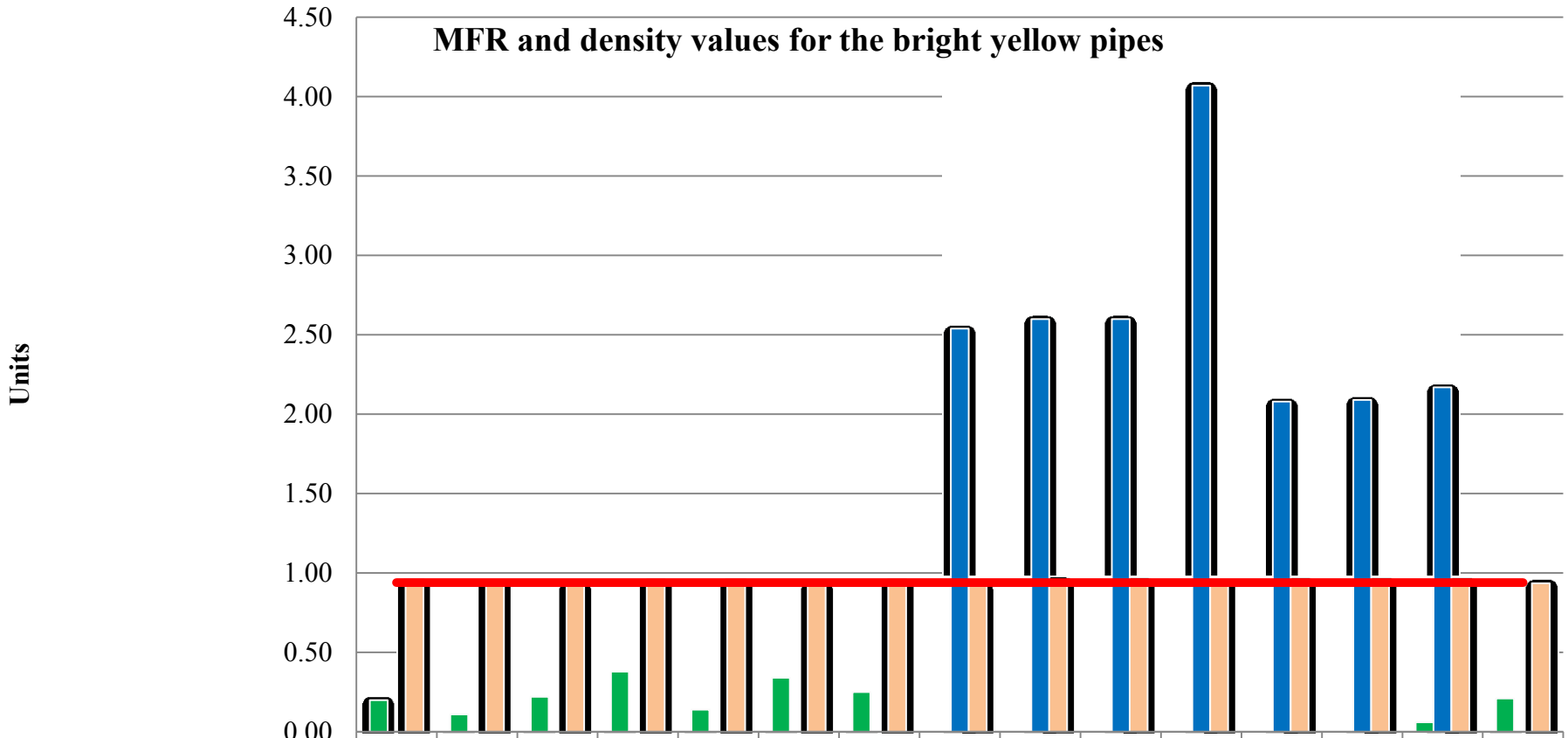
Table 4. Identification of the bright yellow PE pipes

Exova Code	Colour	Identification	MFR 2.16 kg (g/10min)	MFR 10 kg (g/10min)	Density (g/cm^3)
6803	bright yellow	MDPE 1	0.20		0.942
3205 065A	bright yellow	MDPE 1	0.11		0.937
3205 094C	bright yellow	MDPE 1	0.22		0.923
3205 109D	bright yellow	MDPE 1	0.38		0.940
3205 122	bright yellow	MDPE 1	0.14		0.943
3205 126A	bright yellow	MDPE 1	0.34		0.924
3205 127A	bright yellow	MDPE 1	0.25		0.942
3205 139A	bright yellow	MDPE 2		2.54	0.918
3205 139B	bright yellow	MDPE 2		2.60	0.949
3205 139C	bright yellow	MDPE 2		2.60	0.947
3205 139D	bright yellow	MDPE 2		4.07	0.937
3205 141A	bright yellow	MDPE 2		2.08	0.947
3205 141C	bright yellow	MDPE 2		2.09	0.948
3205 141D	bright yellow	MDPE 1	0.06	2.17	0.948
PE80	bright yellow	MDPE 1	0.21		0.936

The 3205 141D pipe material was analysed successfully using both loads (2.16 and 10 kg) and was found to have MFR values of 0.06 and 2.17 g/10min for the respective load values of 2.16 and 10 kg. Therefore one could assume that the pipes that have a MFR value close to 2.17 g/10min for a 10 kg load used would have an MFR value inferior to 0.06

g/10min if a 2.16 kg load was used. This would be the case for the pipe 3205 139A, 139B, 139C, 141A and 141C.

In Figure 23, the density and MFR values acquired in the laboratory are compared with the expected MFR and density values for the tan PE pipes.



	6803	3205 065A	3205 094C	3205 109D	3205 122	3205 126A	3205 127A	3205 139A	3205 139B	3205 139C	3205 139D	3205 141A	3205 141C	3205 141D	PE80
MFR 2.16 kg (g/10min)	0.20	0.11	0.22	0.38	0.14	0.34	0.25							0.06	0.21
MFR 10 kg (g/10min)								2.54	2.60	2.60	4.07	2.08	2.09	2.17	
Density (g/cm3)	0.942	0.937	0.923	0.94	0.943	0.924	0.942	0.918	0.949	0.947	0.937	0.947	0.948	0.948	0.936
Expected density (g/cm3)	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940	0.940

Figure 23. MFR and density values for the bright yellow pipe

3.1.1.2.1 *Identification of pale yellow pipe samples*

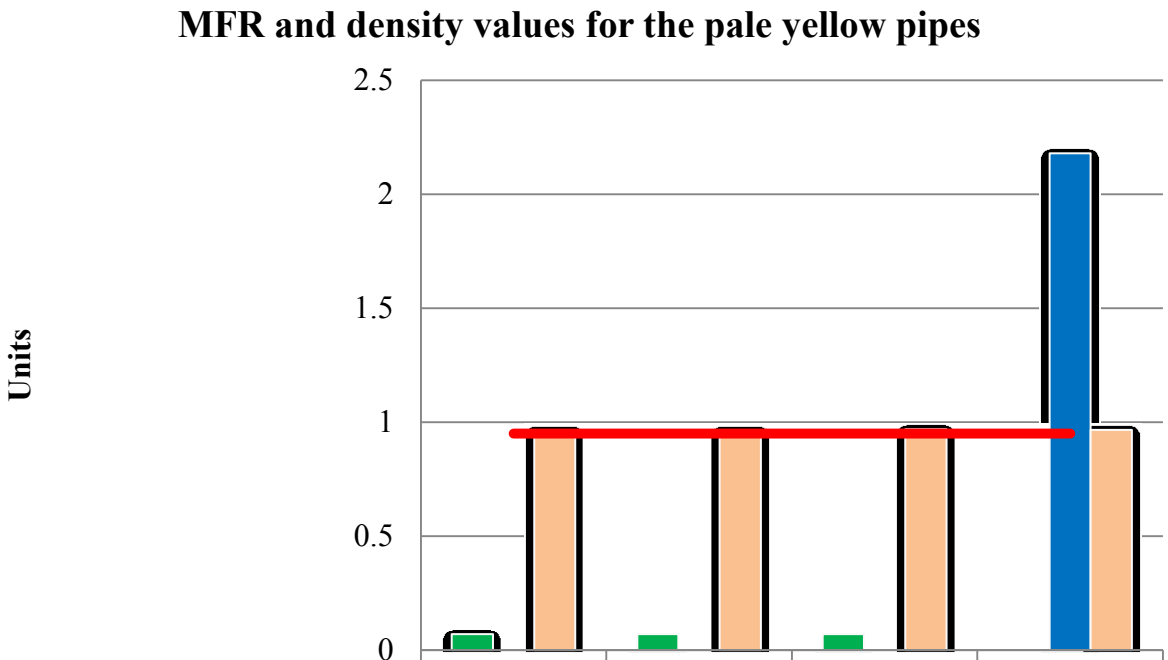
The pale yellow pipes had high density values (0.964-0.969 g/cm3) in the range attributed to HDPE material. Hence pipes 3205 58, 95 and 141E were identified as the HDPE material; see Table 5.

Table 5. Identification of the pale yellow PE pipes

Exova Code	Colour	Identification	MFR 2.16 kg (g/10min)	MFR 10 kg (g/10min)	Density (g/cm^3)
3205 058-1	pale yellow	HDPE	0.07		0.964
3205 058-4	pale yellow	HDPE	0.07		0.964
3205 095	pale yellow	HDPE	0.07		0.969
3205 141E	pale yellow	HDPE		2.18	0.966

It is worth nothing that the MFR value for the HDPE material is very low for a 2.16 kg load used. The MFR value for pipe 141E was too low to be measured using the 2.16 load and had to be analysed with a 10 kg load. A value of 2.18 g/10min was found. The value obtained with the BS1133 condition 190/2.16 would have been lower than 0.06 g/10min if the measure was possible. The MFR gave information on the viscosity of the HDPE but only the density was used to identify the material type.

In Figure 24, the density and MFR values acquired in the laboratory are compared with the expected MFR and density values for the tan PE pipes.



	3205 058-1	3205 058-4	3205 095	3205 141E
MFR 2.16 kg (g/10min)	0.07	0.07	0.07	
MFR 10 kg (g/10min)				2.18
Density (g/cm3)	0.964	0.964	0.969	0.966
Expected density (g/cm3)	0.950	0.950	0.950	0.950

Figure 24. MFR and Density values comparison for the pale yellow pipes

3.1.1.2.2 *Identification of green yellow pipe samples*

Table 6. Identification of the green yellow PE pipes

Exova Code	MFR 2.16 kg (g/10min)	Density (g/cm3)	Identification
3205 6B	1.20	0.941	Unknown Alathon grade
3205 7	1.17	0.940	Unknown Alathon grade
3205 9A	1.18	0.934	Unknown Alathon grade
3205 12	1.20	0.943	Unknown Alathon grade
3205 13	1.24	0.943	Unknown Alathon grade
3205 19	1.15	0.940	Unknown Alathon grade
3205 21A	1.15	0.940	Unknown Alathon grade
3205 066A	1,11	0,941	Unknown Alathon grade
3205 11	1.07	0.939	Unknown Alathon grade
3205 1A	1.19	0.945	Unknown Alathon grade
3205 1B	N/A	N/A	Unknown Alathon grade
3205 2	1.08	0.941	Unknown Alathon grade
3205 4	1.20	0.943	Unknown Alathon grade
3205 31B	1,08	0,942	Unknown Alathon grade
3205 32A	1,35	0,946	Unknown Alathon grade
3205 34	1,25	0,944	Unknown Alathon grade
3205 35	1,23	0,945	Unknown Alathon grade
3205 36-1A	1,20	0,945	Unknown Alathon grade
3205 37F	1,16	0,946	Unknown Alathon grade
3205 041	1,10	0,943	Unknown Alathon grade
3205 42A	1,36	0,943	Unknown Alathon grade
3205 43A	1,37	0,946	Unknown Alathon grade
3205 44A	1,07	0,944	Unknown Alathon grade
3205 45D	1,28	0,943	Unknown Alathon grade
3205 53A	1,03	0,944	Unknown Alathon grade
3205 57	1,20	0,945	Unknown Alathon grade
3205 64G	1,08	0,948	Unknown Alathon grade
3205 67A	1,25	0,944	Unknown Alathon grade
3205 78A	1,18	0,948	Unknown Alathon grade
3205 81 A	N/A	0.946	Unknown Alathon grade
3205 83A	1,17	0,942	Unknown Alathon grade

Exova Code	MFR 2.16 kg (g/10min)	Density (g/cm3)	Identification
3205 84A	1,17	0,944	Unknown Alathon grade
3205 85A	1,18	0,943	Unknown Alathon grade
3205 86A	1,18	0,942	Unknown Alathon grade
3205 88	1,28	0,942	Unknown Alathon grade
3205 90A	1,25	0,944	Unknown Alathon grade
3205 92A	1,29	0,940	Unknown Alathon grade
3205 94A	N/A	0.943	Unknown Alathon grade
3205 103B	1,20	0,946	Unknown Alathon grade
3205 106A	1,25	0,946	Unknown Alathon grade
3205 109C	N/A	0.950	Unknown Alathon grade
3205 110A	1,07	0,950	Unknown Alathon grade
3205 115A	1,44	0,945	Unknown Alathon grade
3205 116	1,18	0,945	Unknown Alathon grade
3205 118A	1,15	0,941	Unknown Alathon grade
3205 118D	1,16	0,946	Unknown Alathon grade
3205 119A	1,16	0,943	Unknown Alathon grade
3205 147	1,07	0,943	Unknown Alathon grade
3205 148	1,28	0,947	Unknown Alathon grade
3205 150	1,19	0,945	Unknown Alathon grade
3205 161A	1,17	0,944	Unknown Alathon grade
3205 163B	1,17	0,944	Unknown Alathon grade
3205 177	1,18	0,942	Unknown Alathon grade
3205 178J	1,16	0,941	Unknown Alathon grade

The green yellow pipes are the most difficult to differentiate in terms of grades using the MFR and density techniques. They could either be Alathon 5043, 5046-C or 5046-U. It is not certain to date to what extent Alathon 5046-C and 5046-U were introduced to the UK, however it is believed that only a small amount was introduced overall. It is therefore most unlikely that these materials are present within the samples provided; that said, the possibility will not be ruled out.

Chain branches were added to the Aldyl A grade 5043 to create the 5046 PE backbone via co-polymerization. Butene was used as a co-monomer for 5043 whereas octane

was used for 5046 C and 5046 U. The site and frequency of chain branches would have affected other aspects of the crystalline/amorphous network such as the size and distribution of spherulites, as well as the nature of the intermediate network of molecules that are between spherulites. The change in comonomer from butane to octene improved the mechanical properties of the Alathon grades. Using butene as co-monomer would have resulted in an "ethyl" side chain structure[10] whereas using octene would have resulted in hexyl side chains. Longer side branching reduces crystallinity and therefore lowers density. So logically, the Aldyl A grades that were made using the octene co-monomers would be expected to have the lowest density. Instead the density at least for the 5046-C theoretically matches the one made out of butane co-monomer (0.939 g/cm^3). As it only takes a small amount of branching to affect the density, it is supposed that a suitable method to reduce considerably the amount of side chains was found at this time. The density was reduced from Alathon 5046-C to 5046-U with a value of 0.933 g/cm^3 since more octane co-monomer was added to the structure. The change in co-monomer improved the slow crack growth resistance of the Aldyl A pipes. This was probably due to a greater amount of inter-lamellar tying arising from increased branching.

The amount of side branching can act on the density of the PE molecule. Side branching is the random bonding of short alkyl chains to the main polymer chain. If the frequency of branching exceeds a critical value (assuming uniform distribution along the main chain), crystallisation of chain segments will be prevented completely. As the level of branching is reduced from this critical value it will become possible to form crystal structures with a lamellar thickness limited by the average length of chain between branch points. As the level of branching reduces further the lamellar thickness, and therefore T_m, will increase to a limiting value of ca. 135 °C, corresponding to linear PE (HDPE). As the level of branching decreases the amount of chain which is sufficiently unbranched to be incorporated into a lamellar structure increases – crystalline content therefore increases. Crystalline regions are characterised by areas within the polymer matrix where portions of the polymer chain align themselves in closely packed and very well ordered arrangements of polyhedral-shaped, microscopic crystals called spherulites. The intermolecular spacing is low in these regions. Amorphous regions are described as areas where portions of polymer chains have no definite molecular arrangement and where intermolecular spacing is high.

Polyethylene is a semi-crystalline material. It means that it contains both crystalline

and amorphous regions. Due to the higher free volume in the amorphous regions they are the first point of attack by oxygen leading to degradation. As antioxidants molecules are too bulky to be permitted within the crystalline regions they reside in the amorphous regions. Mercaptans and other additives introduced to the gas supply are also likely to reside within the amorphous region. The smell of mercaptan was particularly strong when conducting thermal analysis such as MFR or DSC on green - yellow pipes.

It is predictable that the density values will not be a great help in terms of differencing the Alathon grades. This is because the density values for the alathon 5043, 5046-C and 5046-U were so close to each other originally (i.e. 0.939, 0.939 and 0.933 g/cm^3, respectively).

The MFR values for these three grades do not show sufficient variation to allow an efficient identification using the MFR measurement technique. The expected MFR values were all originally around 1.1 g/10min, except for the Alathon 5043 for which the MFR value was originally 1.2 but later changed to 1.1 g/10min. Also, thermo-oxidative degradation of the material is expected to have changed the MFR values causing them to either increase or decrease, depending on the dominant mode of degradation. This effect was studied previously for the tan pipe material.

The molecular weight distribution is very dependent upon the type of process used to manufacture the particular polyethylene resin. Resins that have the same average density and MFR such as Alathon 5043 and 5046-C can have very different molecular weight distributions. In order to properly differentiate these grades, it would be useful to find out their MWD using gel permeation chromatography (GPC) and viscometry. Another way would be to compare their performance in slow crack growth test. For this study, SIS was used instead. If the characterisation is successful SIS could be a good alternative to more expensive methods of MWD determination when MFR, density and mechanical testing are not appropriate.

3.1.2 Stepwise isothermal segregation

3.1.2.1 Normal stepwise isothermal segregation curve

The melting seen during the heating step of the OIT did not allow a differentiation of

the grades, as shown in Figure 25. The samples believed to be pale yellow HDPE, tan Aldyl A and bright yellow MDPE showed similarities, whereas they are known to have different material structures.

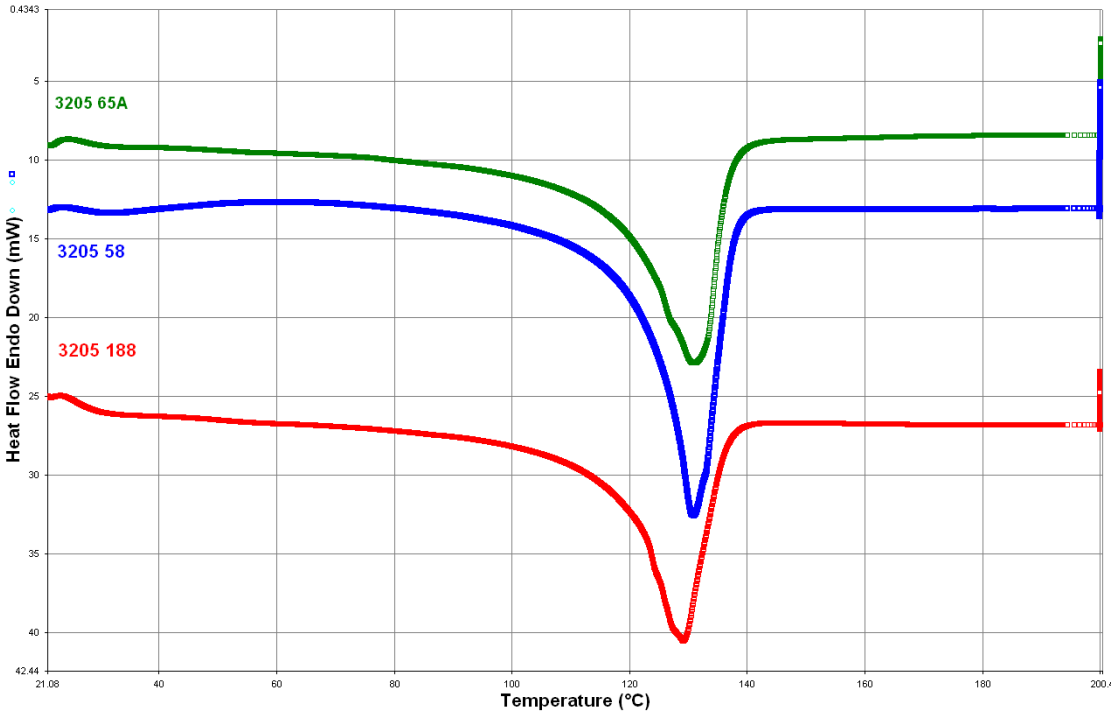


Figure 25. OIT method: : Melting peak from the middle surface of pipe 3205 188 (believed to be tan Aldyl A), 3205 65A (believed to be a different type of MDPE) and 3205 58 (believed to be HDPE)

The SIS technique generates distinct and almost resolved thermal fractions with quasi separated melting peaks. In Figure 26, the SIS traces of a HDPE, MDPE and Aldyl A allow these different materials to be identified. The pale yellow HDPE, shows a high intensity peak at around 129°C and a medium intensity peak at around 121°C. Tan Aldyl A sample 3205 188 shows a high intensity peak at 128°C, a medium intensity peak at around 121°C and a low intensity shoulder at around 114°C. An early MDPE, 3205 65A, two high intensity peaks at around 129°C and 131°C, a medium intensity peak at around 121°C and a low intensity shoulder at around 115°C. Each melting fraction can be associated to an average lamellar thickness[57]. Lamellae are formed from polymer chains folding back and forth together perpendicularly to the lamellae surface. For semi crystalline polymers, the lamellae thickness is dependent upon the crystallisation conditions (crystallisation temperature and annealing time). Increasing the annealing time could probably allow a better resolution between melting fractions.

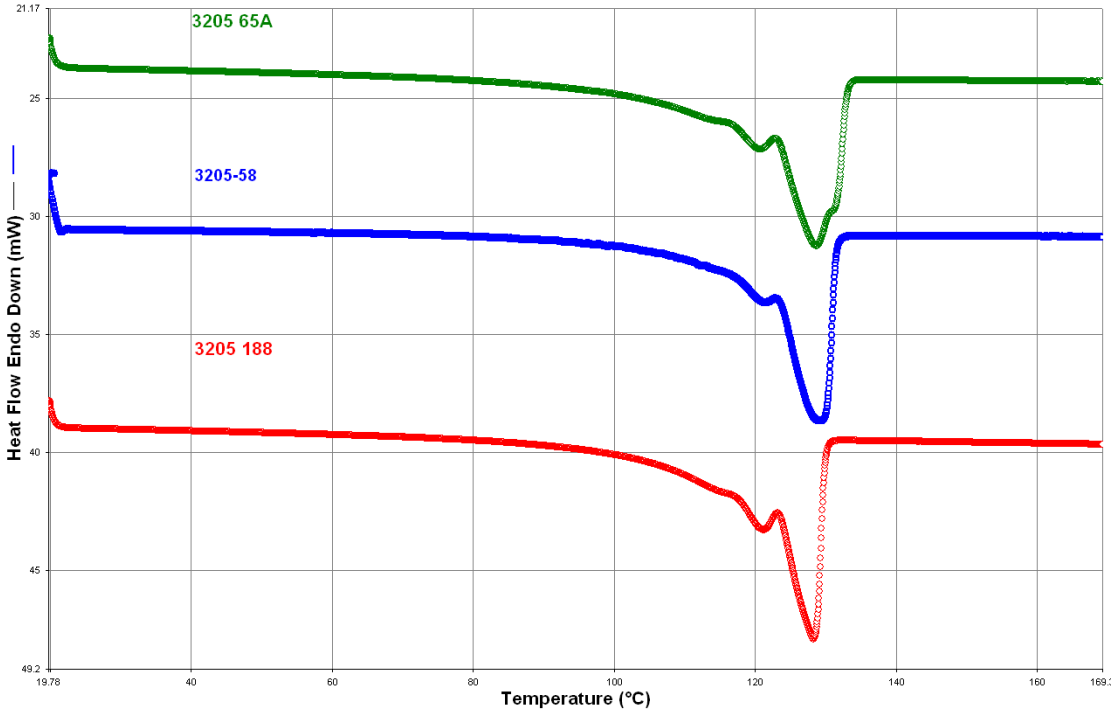


Figure 26. SIS method: Traces from the middle surface of pipe 3205 188 (believed to be tan Aldyl A), 3205 65A (believed to be another type of MDPE) and 3205 58 (believed to be HDPE) after crystallisation treatment.

The annealing process resulted in the molecular segregation of PE chains with varying levels / distributions of short chain branching[58]. Therefore the SIS method was a better characterisation method for identifying the different PE gas pipe materials than the melting peak from the OIT of the polymeric material.

3.1.2.2 Differentiation of Alathon materials using the SIS technique

If the SIS technique is providing sufficient resolution to differentiate different types of PE it might also allow a differentiation between the different grades of the same type of PE. The Alathon 5043 differs from the 5040 grade by its increased density and higher molecular weight. The increase in molecular weight would have caused the material to be more viscous by introducing longer chains. Therefore these materials can already be identified by their melt flow rate and so can provide confirmation of the SIS data.

Pipe material 3205 188 believed to be Alathon 5040 showed sharp melting peaks around 128°C, 121°C and a shoulder around 114°C using the SIS technique as shown in Figure 27.

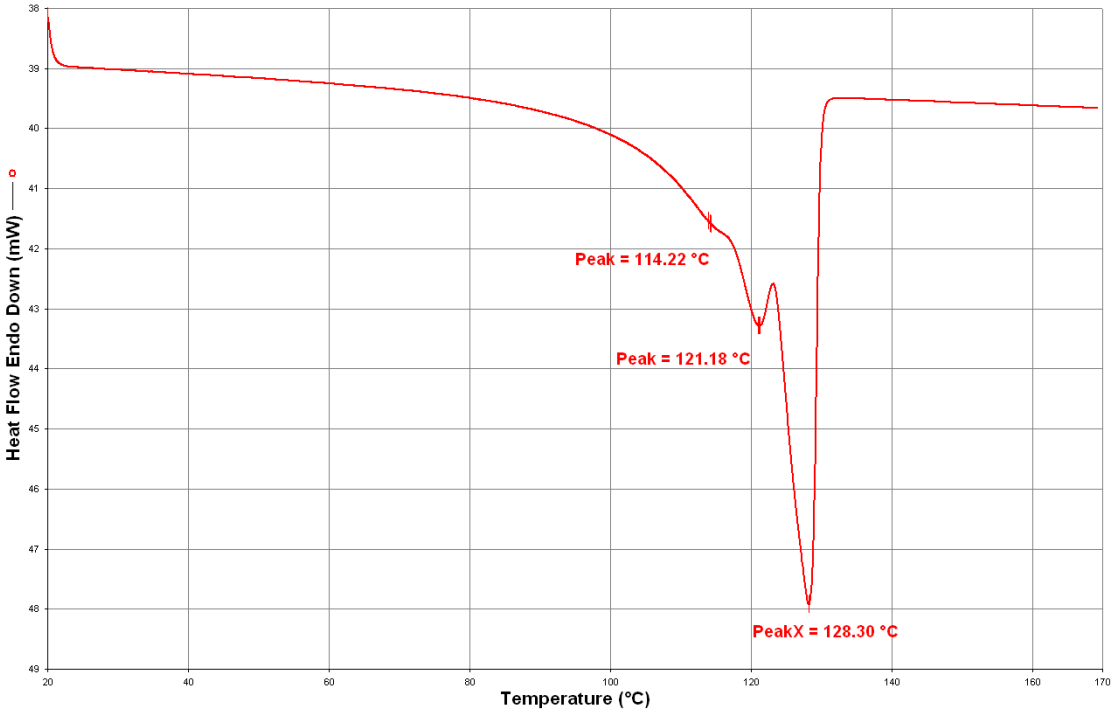


Figure 27. SIS method: melting of 3205 188 – Alathon 5040

Pipe material 3205 184D believed to be an Alathon 5043 showed sharp melting peaks around 130°C and a small peak around 122°C with a negligible shoulder around 114°C as shown in Figure 28.

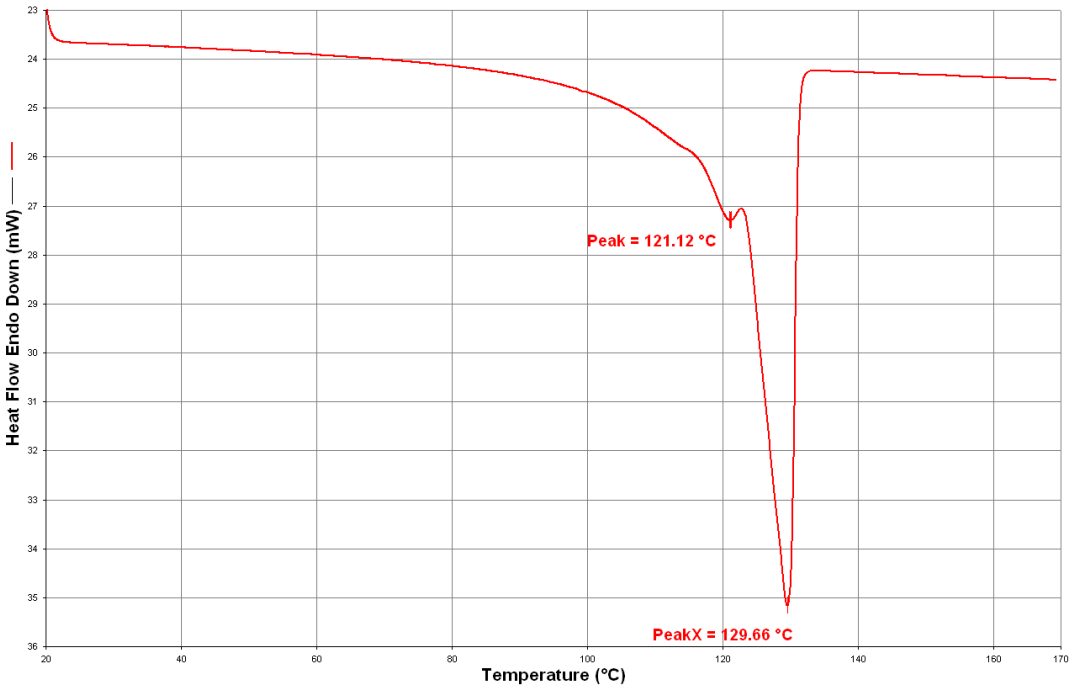


Figure 28. SIS methodd: melting of 3205 184D - Alathon 5043

As the melting point of polymer lamellae increase with thickness[59], the small 2°C increase in the melting portion going from Alathon 5040 to Alathon 5043 could be due to an

increase in the lamellae thickness. The shoulder disappearance is also visible. This could be due to a smaller quantity of thin lamellae present in the Alathon 5043.

3.1.2.2.1 *Identification tan coloured pipe materials using SIS*

The tan pipe material should feature two Alathon grades: the 5040 and the 5043. When analysing the middle untouched surfaces of the old pipes via the SIS technique four trends were observed. Figure 29 features the SIS curves for the tan pipes 24, 68A, 117A and 165.

With the information provided in Table 2, it was possible to date the pipes. Pipes 117A and 165 are the oldest and were manufactured in 1970. They were also excavated in the same area. The reason these samples are showing different SIS patterns is difficult to explain but this may be due to seemingly minor variations in the manufacturing process for pipe 117A. Pipe 117A was found with no remaining antioxidants in its pipe wall after almost 50 years in service. This suggests that no antioxidants were added to the pipe in the first place. It is highly unlikely that the antioxidants would have depleted to zero within the central regions of the pipe wall. Pipes 117 and 165 are identified as the Alathon 5040 from MFR and density testing.

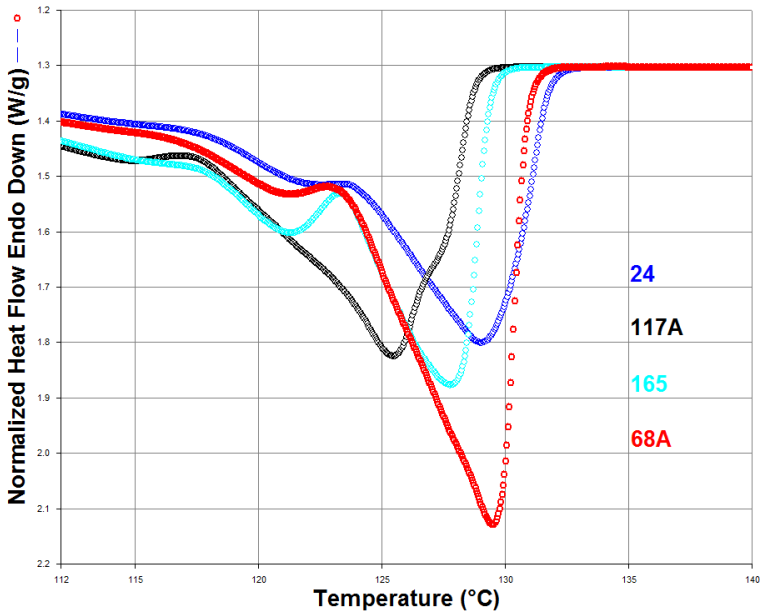


Figure 29. 4 trends observed via the SIS technique for the tan pipe material

Pipe 68 and 24 were both dated from 1971 but came from a different area. As they are made of a relatively newer material they could be Alathon 5043. From Table 1, it is apparent that two versions of Alathon 5043 were produced each, with a different but close in value

melt flow rate (1.2 g/10min for early the version and g/10min 1.1 for the later version). In Table 3, the melt flow rate values for pipe 24 and 68 are expressed with 1.25 g/10min for pipe 24 against 1.07 g/10min for pipe 68. It can then be deduced that pipe 24 is the earlier version on the Alathon 5043 when pipe 68 is the later version.

3.1.2.2.1.1 Identification of tan coloured Alathon 5043 via the SIS technique

Pipe material 3205 50, 51, 49A, 169B and 184D exhibited the same trends as pipe 68, see in Figure 30. This was enough to confirm that they were Alathon 5043. Pipe 169B is a hi tee and pipe 184D a taping tee, their trends were matching completely.

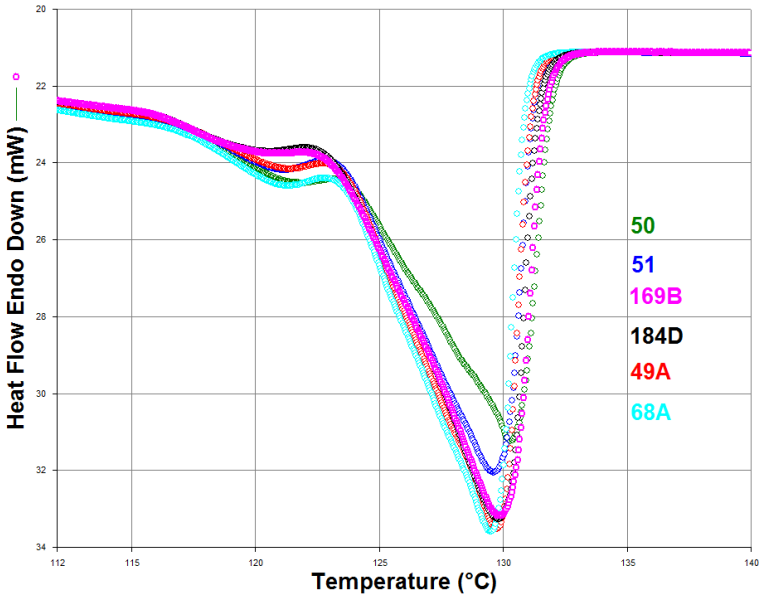


Figure 30. SIS method: comparison of samples believed to be Alathon 5043

It was decided to normalise the Y axis in order to include the weight of the sample in the equation, this removed variations in peak size due to differing sample masses (Figure 31).

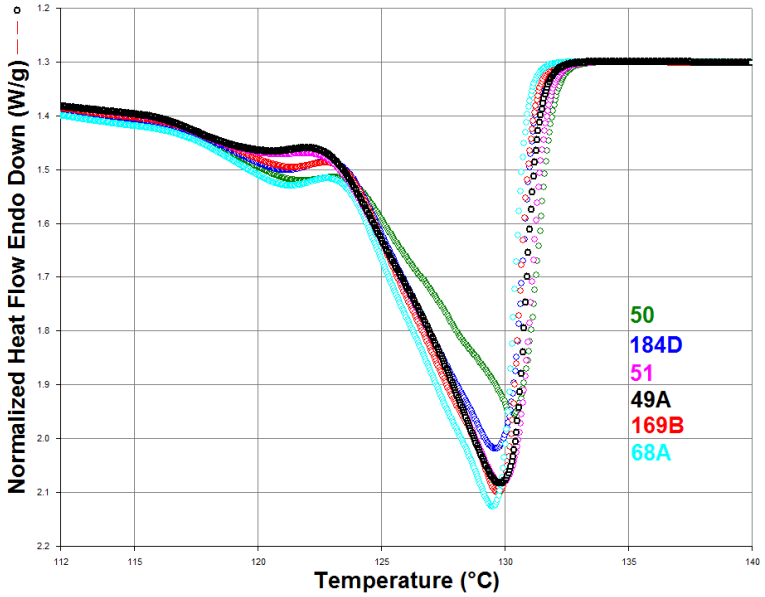


Figure 31. SIS normalised curve: comparison of samples believed to be Alathon 5043

Pipes 49A, 50 and 51 all come directly from the USA. Pipes 68, 169B and 184D were exhumed in different areas of the UK. The thermogram for 49A and 51 are matching completely. 68 and 169B are showing the same general trend except for the small peak around 122°C which is more pronounced then for 49 and 51. Pipe 50 shows the features of the Alathon 5043. The Alathon 5043 melting characteristics are a sharp melting peak around 130°C and a small peak at around 122°C with a negligible shoulder around 114°C. That said a more reliable way to read this data must be found in order to facilitate the identification process using the SIS technique. The SIS technique seems to be a good tool to identify material types of PE regardless of their service location and their age. However the data is not easy to read and it is left to the analyst to find similar features in the SIS curves. This could lead to mistakes, thus a more reliable way of characterising the trends must be found.

The pipes coming from the USA are studied in Figure 32, they are compared with a green yellow metric pipe 53A and the tan tapping tee 169B.

The SIS fingerprint of pipe 49A and 51 overlap and therefore, it can be concluded that they are made of the same material. The SIS fingerprint for 52A, 50 and 53A are unique comparatively to each other. Therefore they may be made of a different material also different from the one used to make pipe 49A and 51.

When comparing the fingerprint of the pipes from America to a tan material identified as the second version of the Alathon 5043 resin, pipes 49A and 51 are the ones showing the most similarities with the tan tapping tee 169B.

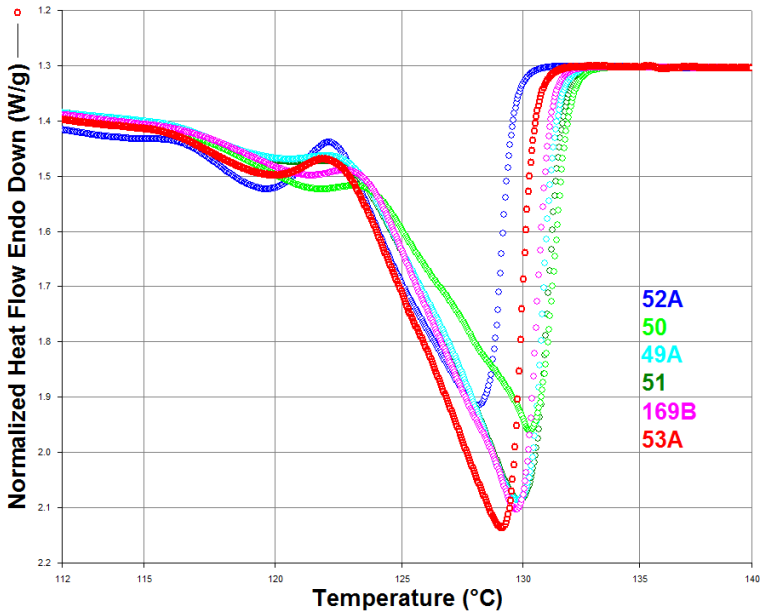


Figure 32. Comparison of samples coming from the USA and a tan pipe 169B

In conclusion the identification of the USA pipe material is difficult because they do not correspond to any of the UK material. Only pipe 49 and 51 showed similarity with the later version of tan Alathon 5043.

3.1.2.2.1.2 Identification of tan coloured Alathon 5040 via the SIS technique

Earlier pipe 24 was confirmed to be the first version of the Alathon 5043. However there was still a concern that this pipe could be made of the Alathon 5040. In Figure 33, it seems clear that the trend adopted by pipe 165 is characteristic to the Alathon 5040 and that this trend is not followed by pipe 24. Two other pipes (187 and 188) show the same trend as pipe 165. Pipe 117A shows a different trend from 165 and 24. Pipe 117A, 165, 187 and 188 were excavated in the same area when pipe 24 was excavated in another area.

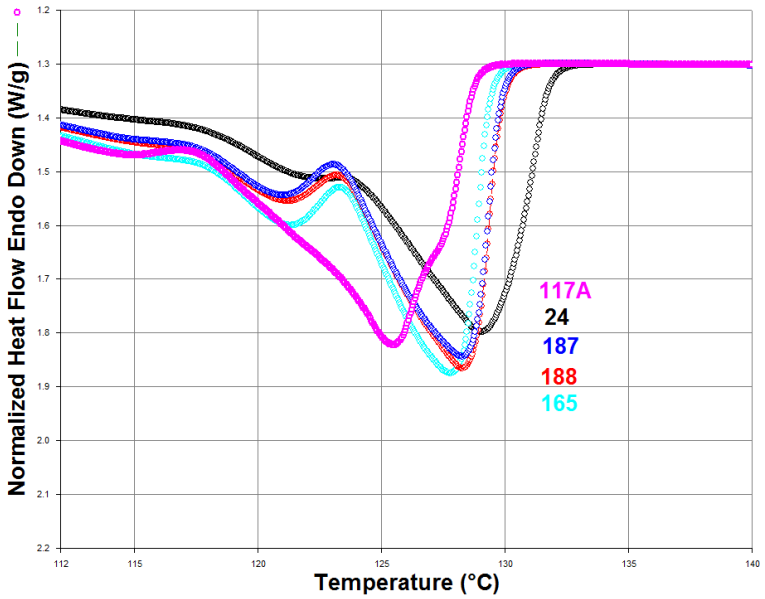


Figure 33. Comparison of samples believed to be Alathon 5040 and pipe 24

In conclusion pipes 165,187 and 188 are confirmed to be made of the Alathon 5040. Although pipe 117A has a completely different curve shape, it is still believed to be the Alathon 5040 from MFR and density results. It is also thought that there were manufacturing problems associated with the production of this pipe leading to the creation of variations in materials produced at this time.

3.1.2.2.2 *Identification of the green yellow coloured Alathon 5043 via the SIS technique*

Three variations of material were recognised when analysing the middle surface of the old green yellow pipes via the SIS technique as shown in Figure 34.

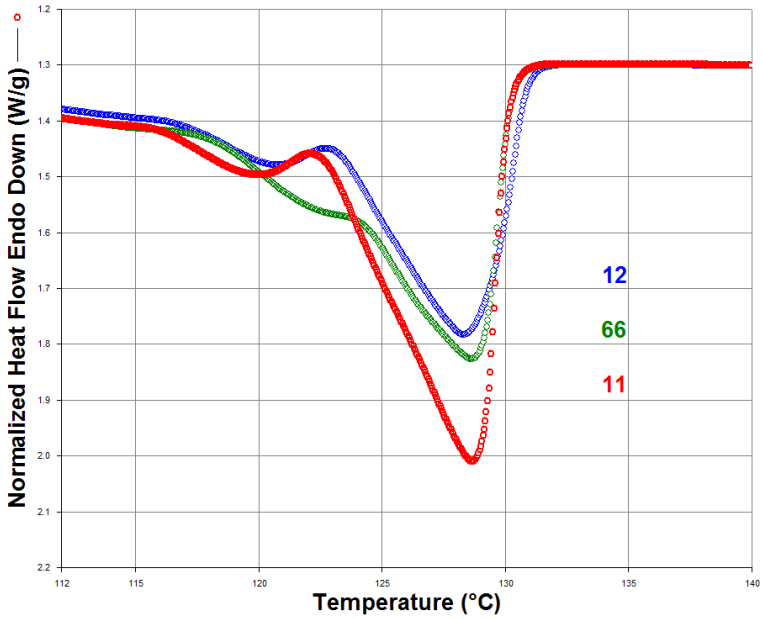


Figure 34. 3 trends observed via the SIS technique for the green yellow pipe material

Using the information from both Table 1 and Table 2 it was possible to find out more about these pipes. First, pipe 11 and 12 were taken from unknown locations in the UK and were manufactured in 1987. These pipes could be the Alathon 5046-C which was being produced between 1983 and 1988 or resulting from manufacturing trials. The second hypothesis is more possible due to the fact that it is not believed to this day that any Alathon 5046 was introduced to the UK soil.

Pipe 66 was excavated from a known location in the UK and manufactured in 1979. This pipe could be made of the Alathon 5043 which was being produced between 1970 and 1983. This pipe might have been part of manufacturing trials. This would explain why its trend is different to the Alathon 5043.

In conclusion, it would seem that all three pipes 11, 12 and 66 might be results of manufacturing trials to improve the Aldyl A grade version produced at their time.

3.1.2.2.2.1 Identification of the Alathon 5043 - first generation - via the SIS technique

Pipe 19 showed the same trend as pipe 12 in Figure 35. Pipe 6B, 21A, 9A, 13 and 7 were showing similar curves to pipe 12 however, the small peak at 122°C was less sharp than for pipe 12. That said the main features of the curve were seen so we can conclude that pipes 6B, 21A, 9A, 13, 7, 12 and 19 are made of the same material. Another interesting fact is that pipes 6B, 21A, 9A, 13, 7 match the trend of the first version of the tan Alathon 5043 showed as pipe 24.

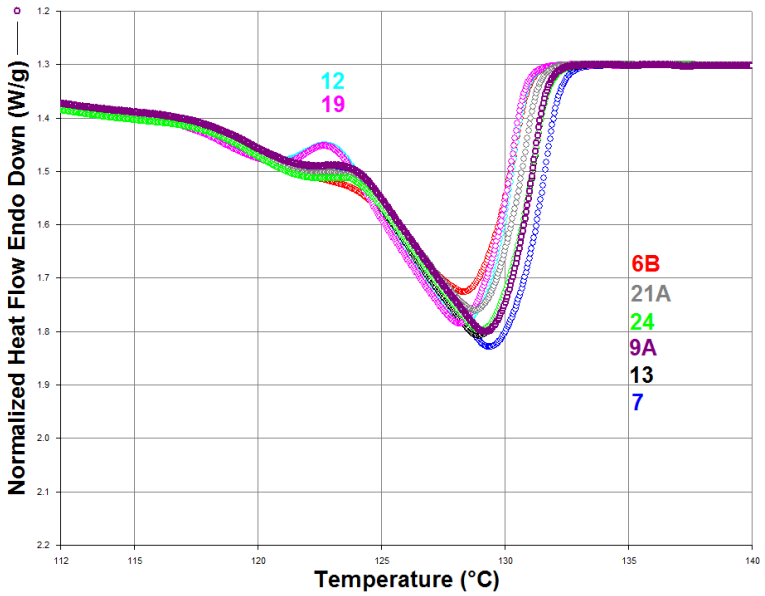


Figure 35. Pipe material showing the same trend as the green yellow pipe 12

Using the information from both Table 1 and Table 2 it was possible to find out more about these pipes. It is interesting to point out that pipe 19 which showed the exact same trend as pipe 12 was manufactured in 1980. It is possible that the year of manufacture of pipe 12 is wrong and that this pipe was actually produced earlier than 1987. Pipes 12 and 19 could be the result of manufacturing trials when producing the Alathon 5043. The area where pipe 12 and 19 were excavated remains unknown.

The area where pipe 21A and 13 were taken from is unknown. Pipe 7 and 9A were taken from the same area (area 1) which is different from the area where pipe 6B (area 2) and 24 (area 5) were taken from.

The year of manufacture for pipes 6B, 21A, 9A, 13 and 7 varies between 1975 and 1981, however they are surprisingly showing the same features as a pipe that was produced in 1971.

To conclude this part the SIS technique can differentiate materials regardless of the area where they come from. Although pipe 12 and 19 are showing some dissimilarity with the other pipe material it was decided to class them in the same group as this would ease the identification process. It may be that these pipes were part of the development and were manufacturing trials. It can also be concluded that pipe 6B, 21A, 9A, 13, 7 seem to have been made of the same resin as the tan pipe 24. This resin would be the first version of the Alathon 5043.

3.1.2.2.2.2 Identification of the Alathon 5043 - second generation - via the SIS technique

The rest of the excavated pipes showed similarities in their SIS trend with pipe 11 as shown in Figure 36. However pipe 11 shows a sharper small peak around 122°C. Pipe 66 is the only pipe showing a SIS curve of its kind. Pipe 66 was found in area 5 and was produced in 1979. This pipe should have been made of the Alathon resin 5043 but does not seem to have followed this trend. A manufacturing fault or trial could have led pipe 66 to have such a unique SIS fingerprint for this material.

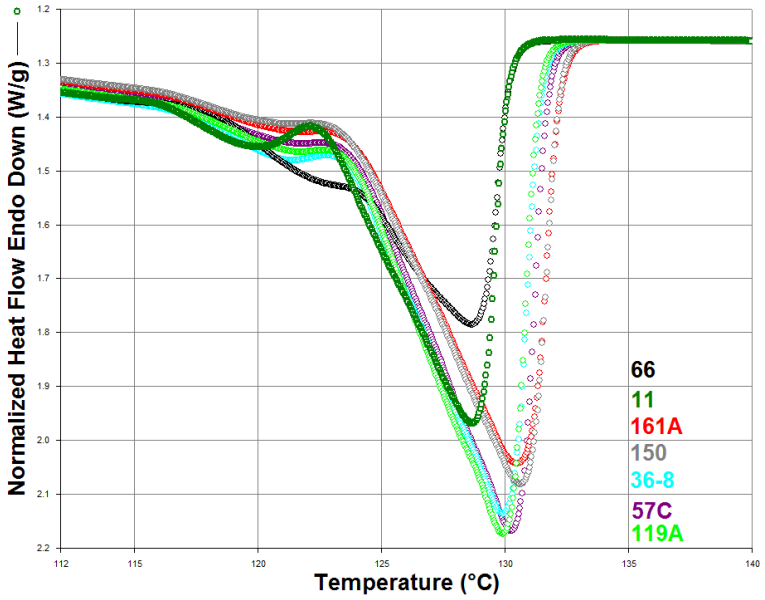


Figure 36. Pipes showing the same SIS trend as pipe 11 and pipe 66

Pipe 11 was manufactured in 1985, and the dimensions of the pipe are metric units. In Table 2, only one other green yellow pipe manufactured after 1983 has metric dimensions. This pipe is 53A and it was manufactured in 1987. The green yellow pipe 103B despite being manufactured in 1988 had imperial dimensions because it came from the USA.

The SIS trend for 103B is identical to most of the green yellow pipes with a curved rather than sharp small peak around 122°C. This trend is also the same observed by the tan top tee material 169B made of the second version of the Alathon 5043 resin.

The SIS trend for 53A and 11 match at least for the shape of the small peak around 122°C. However the area of the large peak is not identical. The year of production of the pipe corresponds with the years of production of the Alathon resin 5046-C. The resin was produced from 1983 to 1988. From the Alathon 5043 to the 5046-C resin there was a change in the co-monomer used resulting in an improvement in slow crack growth resistance. However this resin is not believed to have reached the UK, therefore the most possible reason for the divergence seen within the SIS trends is that pipes 11 and 53A were resulting from manufacturing trial.

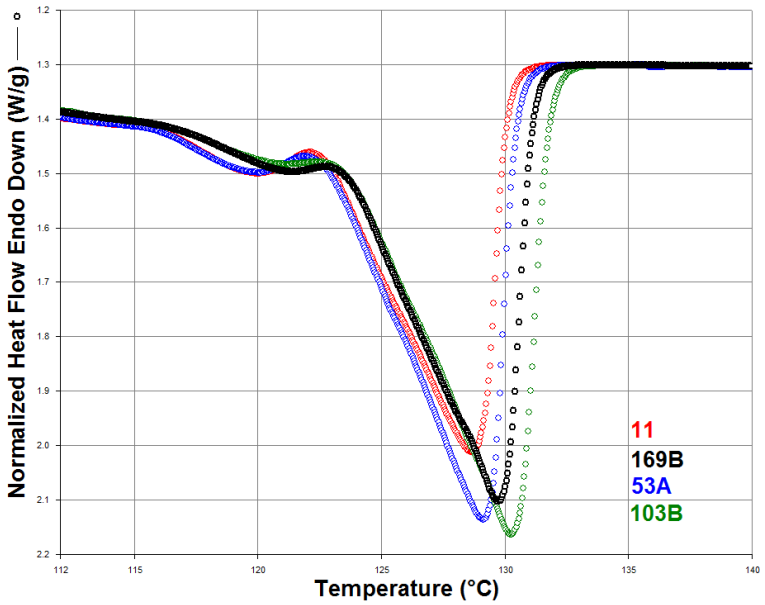


Figure 37. SIS fingerprints for 4 green yellow pipes characteristic of 2 different resin grades

In conclusion the rest of the green yellow pipes were identified as the latest Alathon 5043 material. The SIS trend for this material is the same as the tan pipe made of the same resin. It was found that the shape of the peaks was very important for material identification

but that the area under the peak was not as fundamental.

The green yellow metric pipes 11 and 53A were found to be made of a different material which is probably results of manufacturing trials.

Pipe 66 seems to be a unique material. No other pipes were found with the same SIS fingerprint. This leads the suspicion that a manufacturing fault or trial during the masterbatching process would have led to the creation of a unique material.

3.1.2.2.3 *Identification of the bright yellow coloured MDPE via the SIS technique*

Bright yellow pipe materials were sourced from various European suppliers from the late 70s. In Figure 38, three separate pipes coming from the same area show completely different SIS fingerprints.

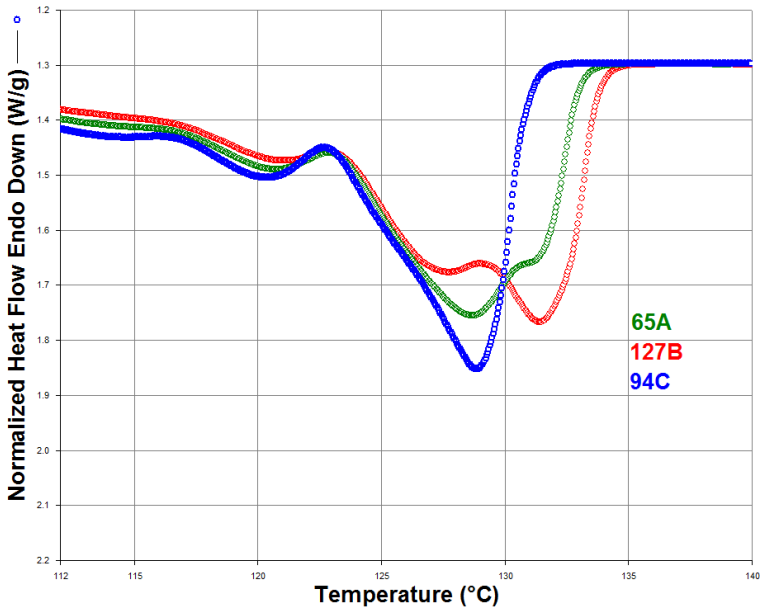


Figure 38. SIS fingerprints for 3 bright yellow pipes from the same area

The SIS fingerprint for 139B and C are match each other perfectly as shown in Figure 39. The fingerprint for section A is a bit offset, but this is negligible. The pipes were found in the same area and their manufacture date is unknown. They have the same diameter and they can all be expected to share the same properties. Since the curves match completely it can even be suggested that the pipe were all made from the same batch.

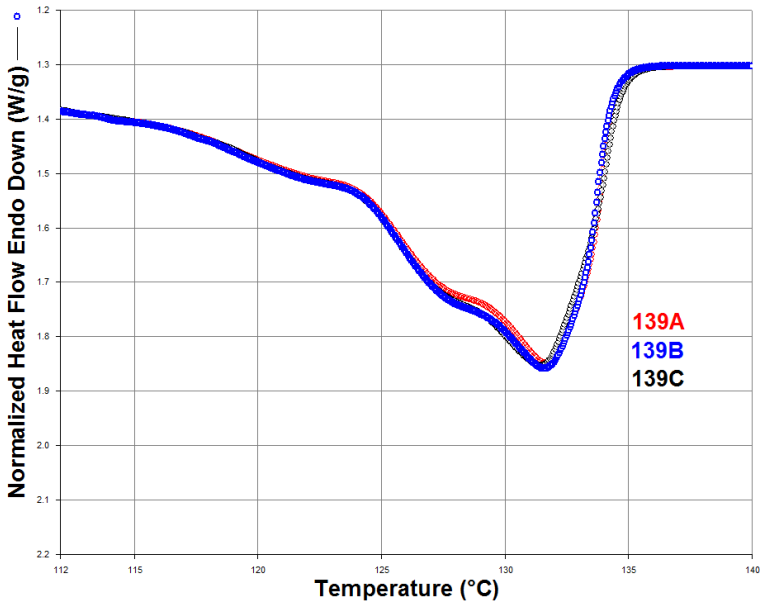


Figure 39. SIS fingerprint for bright yellow pipe 139A, 139B and 139C

The SIS fingerprint for 141A and 141C are matching perfectly as shown in Figure 40. Pipe 141D's SIS trend does not match the first two perfectly however the general curve shape is respected. The bright yellow pipes were found in the same area. It seems that part A and C were produced in the same manner and that is the reason why the SIS fingerprints are the exact same. Table 2 contains information about the pipe diameter. The diameter of the bright yellow pipe 141D was smaller (1 inch SDR 11) than that of samples 141A and C (2 inch SDR 11). SIS would not be able to sense changes in processing technique going from 141 A and C to D because the processing conditions are erased before the annealing process takes place.

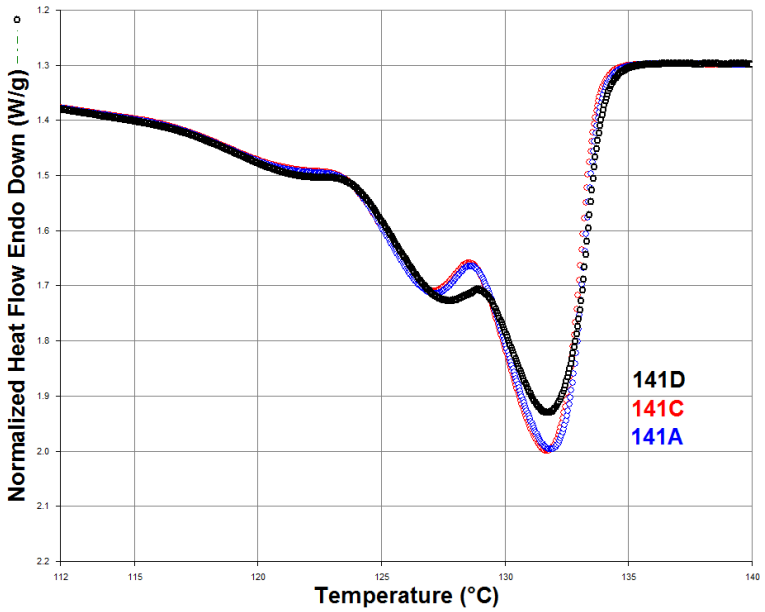


Figure 40. SIS fingerprint for bright yellow pipe 141A, 141C and 141D

The SIS fingerprint for 109D and 127A are shown in Figure 41. The bright yellow pipes were not found in the same area nevertheless they seem to have been made from the same resin. The SIS fingerprints do not exactly match but are very similar despite the pipe diameters differing by a factor of almost five. Pipe 109D has the smallest diameter (1 inch) and pipe 127A is a metric pipe with a larger diameter (125 mm). Despite their difference in pipe diameter, the SIS trend for 127A and 109D are very similar therefore, it can be concluded that the pipe diameter does not affect the SIS results.

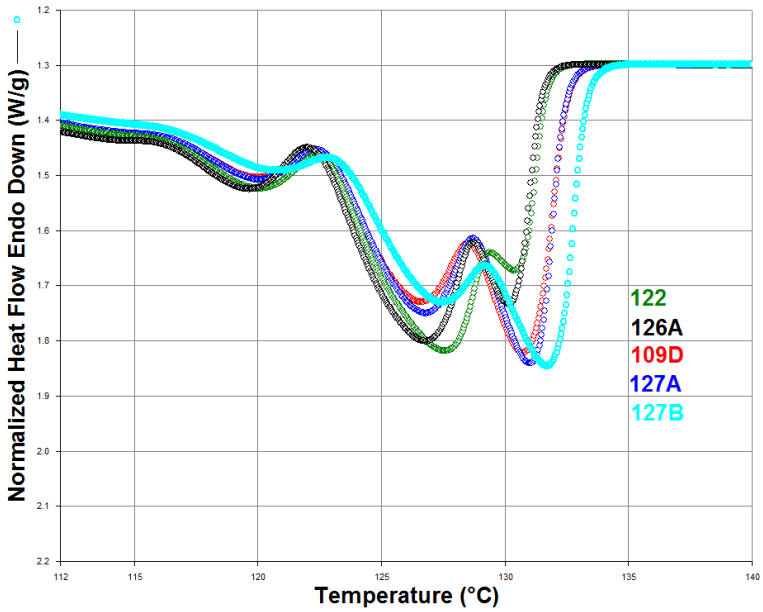


Figure 41. SIS fingerprints of bright yellow pipes 109D, 122, 126A, 127A and 127B

Pipes 122, 127A, 127B and 126A seem to have been made of a different resin material. 127B is in fact a tee fitting so there is a great chance that it would not be made of the same material as 127A.

In conclusion, it seems that the SIS technique cannot detect changes in the material structure relative to its processing conditions. Therefore if the SIS fingerprints are to be used as a reliable technique to identify pipe material after years in service, it is not necessary to record the SIS fingerprint for each pipe diameter made of the same resin.

Although the SIS is differentiating well between HDPE, MDPE and Aldyl A materials it seems that differentiation between the Aldyl A materials is still complex if there is no reference fingerprints to them compare to. It was down to the expertise and experience of the analyst to define the peaks allowing the identification to take place.

3.1.2.2.4 *Identification of pale yellow coloured HDPE via the SIS technique*

The SIS fingerprints for 95 and 58-4 are very similar, as shown in Figure 42. The area where the pale yellow pipes were excavated is unknown. The pipes were of the same diameter and were produced in the same year. Both pipes were produced from the same resin but different processing conditions could have led to a slight change in the material structure.

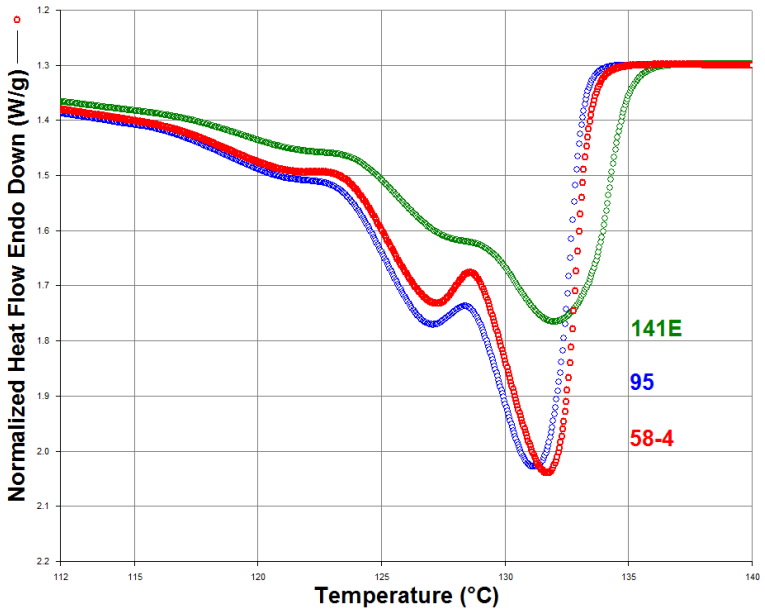


Figure 42. SIS fingerprints of three pale yellow pipes 58-4, 95 and 141E

The SIS fingerprint for the pale yellow pipe 141E is showing a different trend from pipe 95 and 58-4. This pipe is made from a different resin than the first two pipes.

In conclusion unknown factors can affect the material structure. It would be interesting to study the variables affecting the material structure to which the SIS technique is responsive.

It is important to find an even better way to separate the peaks in order to ease the process of peak detection. It was proposed to derivate the SIS curve in an attempt to provide better peak separation.

3.1.2.3 First derivative stepwise isothermal segregation curve

The SIS testing was repeated several times for some of the green yellow Aldyl A, the

tan Aldyl A and the pale yellow HDPE material in order to check for consistency within the results. Peak temperatures were taken from the first derivative of the SIS curves then compared between pipe sections. The same process was also conducted for the HDPE.

The segregation between peaks for the different pipe sections analysed via the SIS technique was very distinct after derivation of the normalised SIS curve. Even though the derivative peaks did not correspond to the normal SIS peaks they were repeatable and much easier to evaluate. The area under the derivative peaks was easily isolated and calculated to allow the percentage ratio to be found.

3.1.2.3.1 *Identification of the green yellow coloured Aldyl A via the SIS derivative method*

The green yellow pipes 36 and 57 as well as one tan pipe material, 68, were analysed using the SIS method. The normal SIS fingerprints of the three pipes were very similar however the shoulder temperatures at around 110°C were difficult to identify. Using the normal SIS fingerprint it was only possible in some cases to record the bigger peaks occurring at around 120 and 130 °C. The first derivative curve featured a total of 5 peaks for the fingerprints of these three materials. Small peaks with a ratio below 3% were detectable using the derivative of the SIS curve. These peaks were usually between the temperature ranges 122-123 and 126-127°C. Bigger derivative peaks occurred around 115-116, 128-129 and 130-131 °C. The percentage ratio for the derivative peak areas in the 130-131 range were the most consistent between pipe sections, therefore the biggest attention was given to this ratio when comparing the pipes for classification. Pipe 36, 57 and 68 showed percentage ratios of 76-80% for all of their replicates. In Table 7 the green yellow pipes materials are identified. The peaks in the 125-126 and 127-128 ranges were ignored because of their negligible values.

Pipe 12 and pipe 19 were showing matching normal SIS fingerprints. Therefore they were considered to have been made of the same resin. They should be expected to share the same properties. Their density and melt flow is in fact very close. The pipe made with the first version of the Alathon 5043 resin (6B, 7, 9A, 12, 13, 19 and 21A) all feature MFR values between 1.15 and 1.24 g/10min. The first version of the Alathon 5043 has a characteristic MFR value of 1.2 g/10min. Pipe 9A has a low density of 0.934 and the other pipes made of the same material have a density between 0.940 and 0.943 g/cm^3. The SIS

derivative fingerprint for the first version of the green yellow pipe 9A produced with the Alathon 5043 resin is shown in Figure 48. This version of the resin features only three peaks on the SIS derivative curve.

Pipe 66 was categorised as been an unique material and featured the same MFR and density value as the pipes made with the second version of the Alathon 5043 resin. Without the SIS technique it would have being difficult to recognise that pipe 66 was not made of the same resin as the rest of the excavated pipes because its MFR and density results do not show its individuality. The SIS derivative fingerprint of the unique green yellow pipe material 66 is shown in Figure 49.

Pipe 11 was believed to be the result of manufacturing trials. Again the pipe material featured the same MFR and density value as the pipes made with the second version of the Alathon 5043 resin. Again if the SIS was not conducted the material used for the manufacture of pipe 11 could have been mistaken with the second version of the Alathon 5043 because its MFR and density results do not show its individuality. The SIS derivative fingerprint of the unique green yellow pipe material is shown in Figure 50.

The rest of the green yellow pipes believed to have been made of the second version of the Alathon resin 5043 featured MFR values between 1.00 and 1.25 g/10min for the majority. A few pipes (32A, 42A, 43A, 88, 92A, 115A and 148) had a MFR higher than 1.25g/10min. The expected MFR for the second generation of the Alathon 5043 is 1.1 g/10min. The increase could be due to oxidative degradation during service. The FTIR and OIT data will be checked thoroughly for those pipes in order to find signs of advanced degradation. The density varied from 0.940 to 0.950 g/cm^3. The SIS derivative fingerprint for a pipe (103B) of the second version of the alathon 5043 grade is shown in Figure 47.

Table 7. SIS derivative peaks for green yellow pipe material

Exova Code	MFR 2.16 kg (g/10min)	Density (g/cm3)	Identification	SIS derivative peak temperature		
3205 6B	1.20	0.941	Alathon 5043 – 1st version	116	123	130
3205 7	1.17	0.940	Alathon 5043 – 1st version	116	123	132
3205 9A	1.18	0.934	Alathon 5043 – 1st version	116	123	131
3205 12	1.20	0.943	Alathon 5043 – 1st version	115	122	130
3205 13	1.24	0.943	Alathon 5043 – 1st version	117	123	131
3205 19	1.15	0.940	Alathon 5043 – 1st version	115	122	130
3205 21A	1.15	0.940	Alathon 5043 – 1st version	117	123	131
3205 066A	1,11	0,941	Unique material	117	123	130
3205 11	1.07	0.939	Unique material	115	122	130
3205 1A	1.19	0.945	Alathon 5043 – 2nd version	116	123	132
3205 1B	N/A	N/A	Alathon 5043 – 2nd version	114	123	132
3205 2	1.08	0.941	Alathon 5043 – 2nd version	115	122	130
3205 4	1.20	0.943	Alathon 5043 – 2nd version	115	122	130
3205 31B	1,08	0,942	Alathon 5043 – 2nd version	115	122	132
3205 32A	1,35	0,946	Alathon 5043 – 2nd version	116	122	131
3205 34	1,25	0,944	Alathon 5043 – 2nd version	115	123	132
3205 35	1,23	0,945	Alathon 5043 – 2nd version	116	123	131
3205 36-1A	1,20	0,945	Alathon 5043 – 2nd version	115	123	131
3205 37F	1,16	0,946	Alathon 5043 – 2nd version	115	122	131
3205 041	1,10	0,943	Alathon 5043 – 2nd version	115	123	131
3205 42A	1,36	0,943	Alathon 5043 – 2nd version	116	123	132
3205 43A	1,37	0,946	Alathon 5043 – 2nd version	115	122	131
3205 44A	1,07	0,944	Alathon 5043 – 2nd version	115	123	131
3205 45D	1,28	0,943	Alathon 5043 – 2nd version	115	122	131
3205 53A	1,03	0,944	Alathon 5043 – 2nd version	115	123	131
3205 57	1,20	0,945	Alathon 5043 – 2nd version	115	123	131
3205 64G	1,08	0,948	Alathon 5043 – 2nd version	115	123	132

Exova Code	MFR 2.16 kg (g/10min)	Density (g/cm3)	Identification	SIS derivative peak temperature		
3205 67A	1,25	0,944	Alathon 5043 – 2nd version	116	122	131
3205 78A	1,18	0,948	Alathon 5043 – 2nd version	116	122	132
3205 81 A	N/A	0.946	Alathon 5043 – 2nd version	115	122	131
3205 83A	1,17	0,942	Alathon 5043 – 2nd version	116	123	131
3205 84A	1,17	0,944	Alathon 5043 – 2nd version	115	122	131
3205 85A	1,18	0,943	Alathon 5043 – 2nd version	115	123	131
3205 86A	1,18	0,942	Alathon 5043 – 2nd version	115	122	131
3205 88	1,28	0,942	Alathon 5043 – 2nd version	116	122	130
3205 90A	1,25	0,944	Alathon 5043 – 2nd version	115	123	132
3205 92A	1,29	0,940	Alathon 5043 – 2nd version	116	122	131
3205 94A	N/A	0.943	Alathon 5043 – 2nd version	115	121	130
3205 103B	1,20	0,946	Alathon 5043 – 2nd version	115	122	131
3205 106A	1,25	0,946	Alathon 5043 – 2nd version	115	122	131
3205 109C	N/A	0.950	Alathon 5043 – 2nd version	115	123	132
3205 110A	1,07	0,950	Alathon 5043 – 2nd version	115	122	132
3205 115A	1,44	0,945	Alathon 5043 – 2nd version	116	123	131
3205 116	1,18	0,945	Alathon 5043 – 2nd version	115	122	131
3205 118A	1,15	0,941	Alathon 5043 – 2nd version	115	122	131
3205 118D	1,16	0,946	Alathon 5043 – 2nd version	115	122	131
3205 119A	1,16	0,943	Alathon 5043 – 2nd version	115	122	131
3205 147	1,07	0,943	Alathon 5043 – 2nd version	115	123	132
3205 148	1,28	0,947	Alathon 5043 – 2nd version	115	122	131
3205 150	1,19	0,945	Alathon 5043 – 2nd version	115	122	132
3205 161A	1,17	0,944	Alathon 5043 – 2nd version	115	123	132
3205 163B	1,17	0,944	Alathon 5043 – 2nd version	115	123	131
3205 177	1,18	0,942	Alathon 5043 – 2nd version	116	122	131
3205 178J	1,16	0,941	Alathon 5043 – 2nd version	116	122	130

3.1.2.3.2 *Identification of the tan pipe coloured Aldyl A via the SIS derivative method*

The tan pipes 49A, 50 and 51 were originally from the USA. They were known to have been made of a different grade than the UK tan pipes although their grade was unknown. When analysing their normal SIS fingerprints, these pipes were found to be made of the second version of the Alathon 5043 resin. However, when analysing their derivative SIS fingerprints another conclusion was reached. The peak at 128°C characteristic of the Alathon 5043 was not found for these pipes. Therefore, it was decided not to categorise them as made of the Alathon 5043. The resin used to produce these pipes remains unknown and was not used in the UK.

Earlier, the conclusion was reached that pipe 51 and pipe 49A were made of the same resin because their fingerprints matched. If they are made of the same resin and have being processed in the same way it is expected for them to share the same properties. Their MFR value are very close to each other (1.07 for 49A and 1.08 g/10 min for pipe 51), see Table 8. Their density value is the same. Pipe 50 normal SIS fingerprint did not match 51 and 49A, and this individuality is also shown by its high MFR value (1.36 g/10min) and its low density result (0.933 g/cm^3). Pipe 52A also features a completely different MFR value of 0.98 g/10min and a low density of 0.934 g/cm^3.

Pipe 24 made with the first version of the Alathon 5043 resin features a MFR value of 1.25 g/10 min. The first version of the Alathon 5043 has a characteristic MFR value of 1.2 g/10 min. It also shows the same three characteristic peaks that the green yellow materials made of the same grade show on their derivative SIS fingerprint. The derivative SIS fingerprint of the first version of the tan pipe 24 produced with the Alathon 5043 resin is shown in Figure 45.

The expected MFR for the second generation of the Alathon 5043 resin is 1.1 g/10min. Pipe 184D and 169D are both fitting. Pipe 184D has a high MFR value (1.29 g/10min) which might be due to degradation. The fingerprint of the second version of the tan pipe 169B produced with the Alathon 5043 resin is shown in Figure 44.

The pipes identified as Alathon 5040 feature a low MFR value in accordance with the expected value (0.935 g/10min). It is also important to note that that the MFR and density results do not suggest that pipe 117A is a unique material. Its MFR and density values are

approximately the same as pipe 188 which was identified as the Alathon 5040. The derivative SIS fingerprint of the tan pipe 188 produced with the Alathon 5040 resin is shown in Figure 43.

The tan Aldyl A pipe 165 was showing peaks at around 121 and 128 °C on the normal SIS thermogram with a unique curve shape. The derivative of the SIS singularised this material even more by identifying three clear peaks in the temperature ranges 116-117, 122-123 and 128-129 °C.

The SIS derivative fingerprint for pipe 117 was unique, featuring 5 peaks with the last two peaks combined into a double peak. The derivative SIS fingerprint of the unique tan pipe material 117A is shown in Figure 46.

Table 8. SIS derivative peaks for tan pipe material

Exova Code	Color	MFR 2.16 kg (g/10min)	Density (g/cm^3)	Identification	SIS derivative peak temperature				
3205 24	tan	1.25	0.941	Alathon 5043 – 1st version	116	124	131		
3205 50	tan	1.36	0.933	USA	115	123	127	129	131
3205 52A	tan	0,98	0,934	USA	115	121	126	129	
3205 53	tan	N/A	N/A	USA	115	121	126	130	
3205 49A	tan	1,07	0,941	USA	115	122	126	131	
3205 51	tan	1,08	0,941	USA	115	122	127	131	
3205 68E	tan	1,07	0,942	Alathon 5043 -2nd version	116	123	126	128	131
3205 169B	tan	1,15	0,941	Alathon 5043 -2nd version	115	122	126	128	131
3205 184D	tan	1,29	0,942	Alathon 5043 -2nd version	115	122	126	128	131
3205 188	tan	1,90	0,936	Alathon 5040	117	123	129		
3205 187	tan	1,98	0,938	Alathon 5040	117	122	129		
3205 165A	tan	2,33	0,939	Alathon 5040	117	123	129		
3205 117A	tan	1,91	0,938	Unique material	116	120	123	126	128

3.1.2.3.3 *Identification of the pale and bright yellow coloured HDPE and MDPE via the SIS derivative method*

The pale yellow HDPE material showed a total of four derivative peaks graduated intensity following the SIS derivative curve. The temperature ranges for the peaks were 114-115, 122-123, 127-128 and 132-133°C. Again the derivative peaks are more representative of the material then the normal SIS peaks.

The HDPE and MDPE materials show the same peaks temperature on their derivative

curves. However they are known to have different structures. It is necessary to compare SIS curve shapes to differentiate the materials. The pipe colour is also a reliable tool to identification.

Pipe sections A, B and D of pipe 141 are made of the same material. The SIS derivative fingerprint differs for section D. The MFR for section D is higher but the density value stayed approximately the same, see Table 9. The SIS derivative fingerprints of the bright yellow material 141A, C and D are shown in Figure 51.

Pipe sections A, B and C of pipe 139 are made of the same material. The SIS fingerprint for section A was a little bit offset comparatively but this was considered to be a negligible effect. The MFR and density values are approximately the same for sections B and C. However the density and MFR results are lower for section A. The SIS technique is able to detect small changes in the material without having to conduct extra MFR or density testing. However the operator must be well trained in what to look for as the changes in the SIS curve shape are not always obvious. The fingerprints of the bright yellow material pipe material 139A, B and C are shown in Figure 52.

Pipes 127A and 109D have the same SIS curve shape however their fingerprints do not match completely. Thus although made of the same material they have very different MFR values, see Table 9. The fingerprints of the bright yellow material pipe materials 127A and 109D are shown in Figure 53.

The fingerprints of the bright yellow material pipe materials 65, 94C, 122, 126 and 127B are shown respectively in Figure 55, Figure 56, Figure 57, Figure 58 and Figure 59. All these pipes are made of a different resin material.

Pale yellow pipes 95 and 58 are HDPE materials made of the same resin. They feature the same approximate density and MFR values, see Table 9. The fingerprints of the pale yellow material pipe materials 95 and 58-4 are shown in Figure 54.

The fingerprint of the pale yellow material pipe material 141E is shown in Figure 60.

Table 9. SIS derivative peaks for the pale and bright yellow pipe material

Exova Code	Color	MFR 2.16 kg (g/10min)	MFR 10 kg (g/10min)	Density (g/cm3)	Identification	SIS curve derivative peak temperature			
3205 65	bright yellow	0.11		0.937	MDPE 1	115	122	128	132
3205 94C	bright yellow	0.22		0.939	MDPE 2	116	122	125	130
3205 109D	bright yellow	0.38		0.940	MDPE 3	115	122	128	132
3205 122	bright yellow	0,14		0,943	MDPE 4	115	122	129	131
3205 126A	bright yellow	0,34		0,924	MDPE 5	115	121	128	131
3205 127A	bright yellow	0,25		0,942	MDPE 3	115	122	128	132
3205 139A	bright yellow		2,54	0,918	MDPE 6	115	123	129	134
3205 139B	bright yellow		2,60	0,949	MDPE 6	115	123	128	134
3205 139C	bright yellow		2,60	0,947	MDPE 6	117	123	128	134
3205 141A	bright yellow		2,08	0,947	MDPE 7	115	123	128	133
3205 141C	bright yellow		2,09	0,948	MDPE 7	115	123	128	133
3205 141D	bright yellow	0,06	2,17	0,948	MDPE 7	115	123	129	133
3205 058-1	pale yellow	0,07		0,964	HDPE 1	115	122	128	133
3205 058-4	pale yellow	0,07		0,964	HDPE 1	115	123	128	133
3205 095	pale yellow	0,07		0,969	HDPE 1	115	122	128	133
3205 141E	pale yellow		2,18	0,966	HDPE 2	115	123	129	134

In order to make sure that the small changes in the SIS derivative thermograms were not due to degradation it was proposed to conduct SIS on aged samples. The SIS tests were conducted directly on the outside exposed surfaces. The SIS of the materials were relatively consistent throughout the pipe length and the pipe thickness. They were also consistent after ageing. This confirmed that the SIS is not sensible to degradation. Or perhaps the pipe were not exposed long enough to allow a sufficient degradation to take place and be detected via the SIS technique.

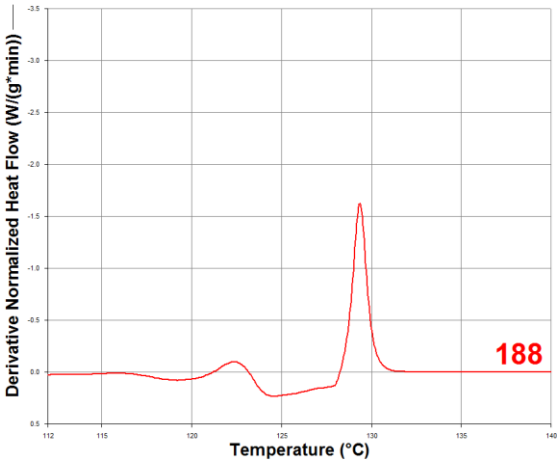


Figure 43. Curve analysis: SIS 1st derivative fingerprint for pipe 188

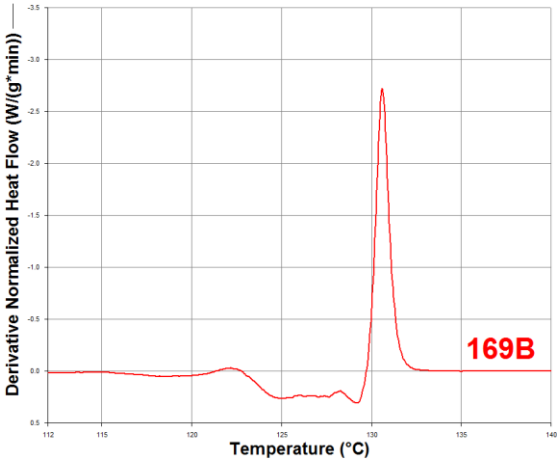


Figure 44. Curve analysis: SIS 1st derivative fingerprint for pipe 169B

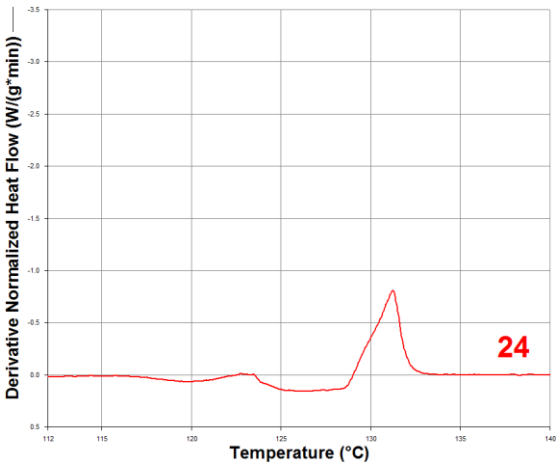


Figure 45. Curve analysis: SIS 1st derivative fingerprint for pipe 24

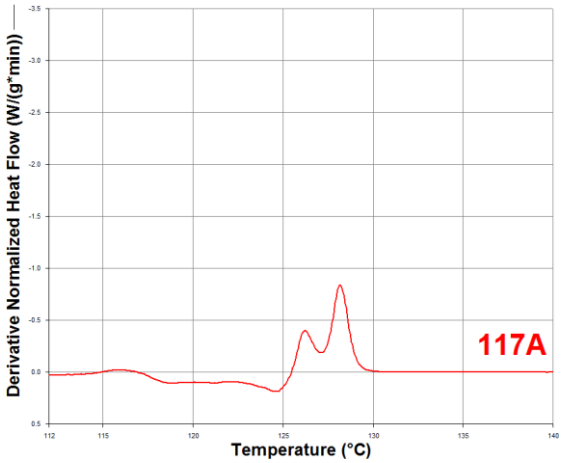


Figure 46. Curve analysis: SIS 1st derivative fingerprint for pipe 117A

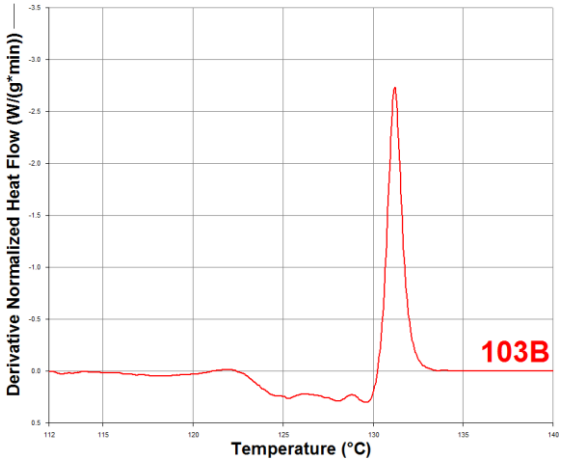


Figure 47. Curve analysis: SIS 1st derivative fingerprint for pipe 103B

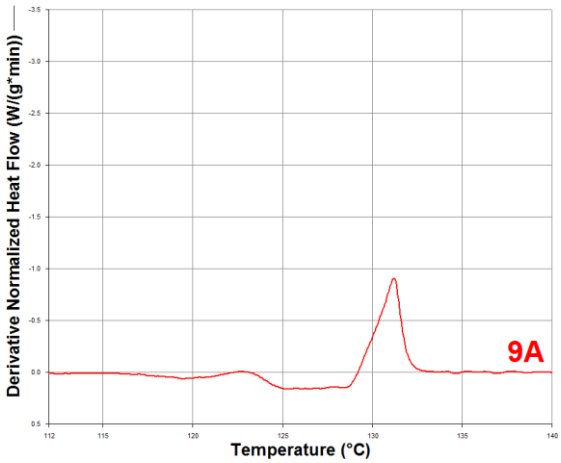


Figure 48. Curve analysis: SIS 1st derivative fingerprint for pipe 9A

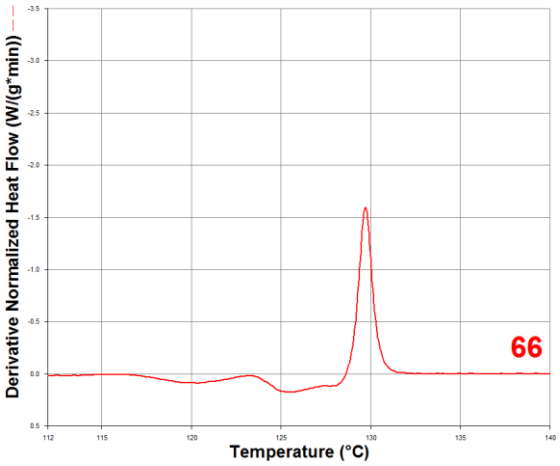


Figure 49. Curve analysis: SIS 1st derivative fingerprint for pipe 66

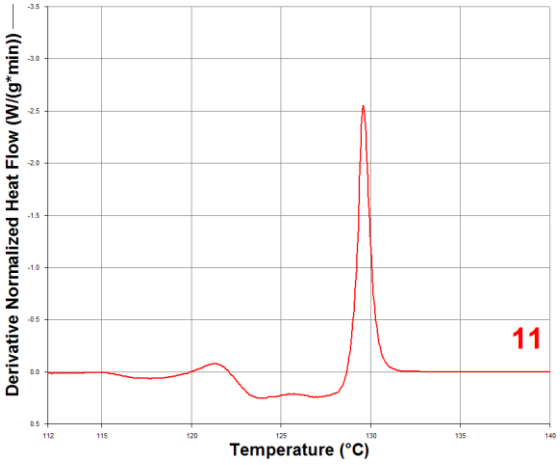


Figure 50. Curve analysis: SIS 1st derivative fingerprint for pipe 11

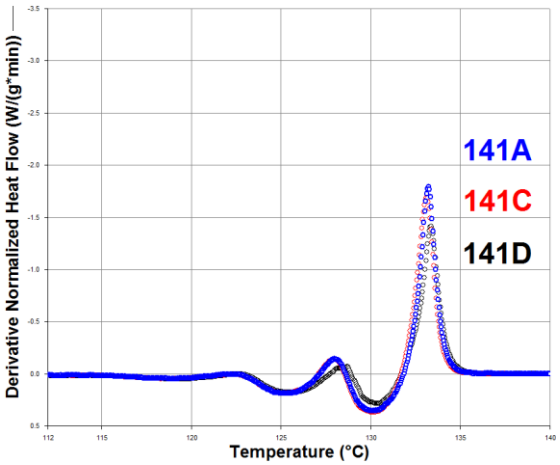


Figure 51. Curve analysis: SIS 1st derivative fingerprint for pipe 141A, C and D

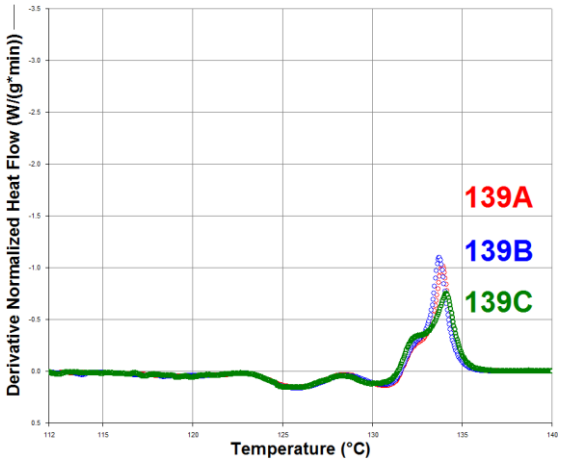


Figure 52. Curve analysis: SIS 1st derivative fingerprint for pipe 139A, B and C

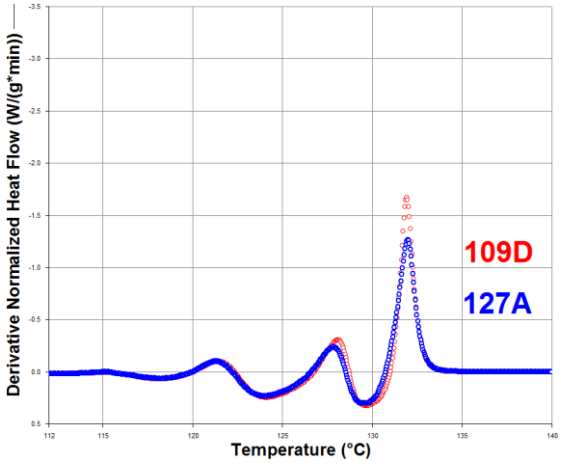


Figure 53. Curve analysis: SIS 1st derivative fingerprint for pipe 109D and 127A

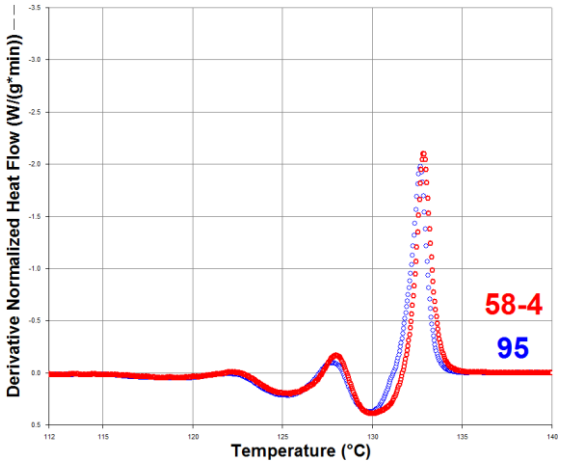


Figure 54. Curve analysis: SIS 1st derivative fingerprint for pipe 58-4 and 95

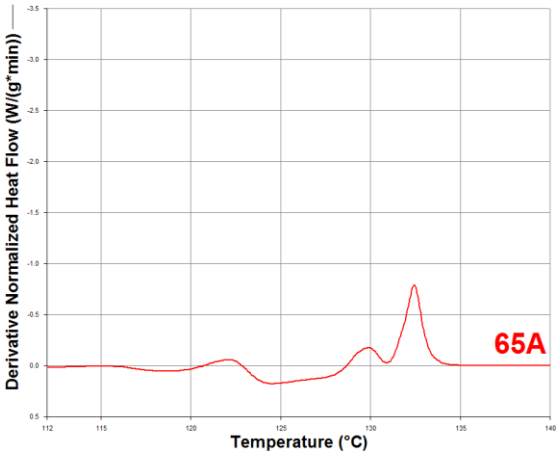


Figure 55. Curve analysis: SIS 1st derivative fingerprint for pipe 65A

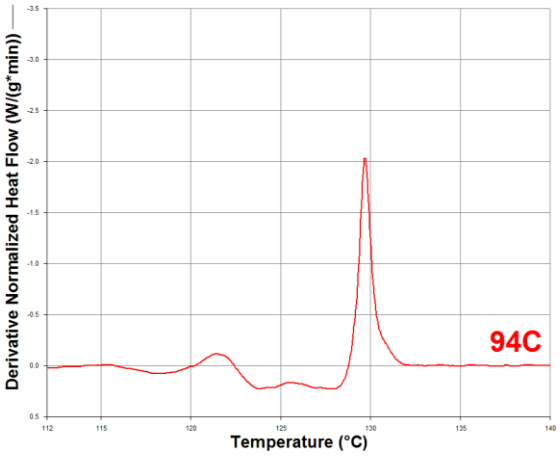


Figure 56. Curve analysis: SIS 1st derivative fingerprint for pipe 94C

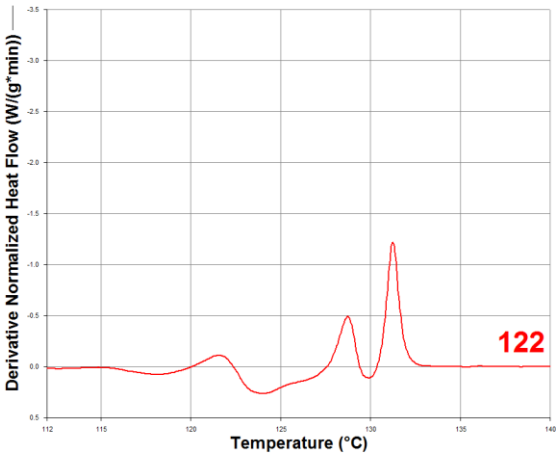


Figure 57. Curve analysis: SIS 1st derivative fingerprint for pipe 122

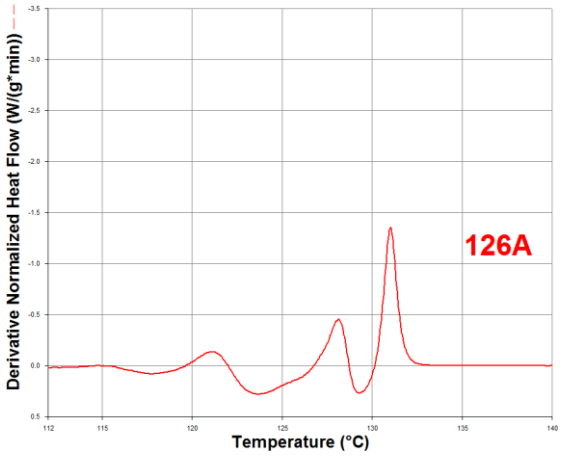


Figure 58. Curve analysis: SIS 1st derivative fingerprint for pipe 126A

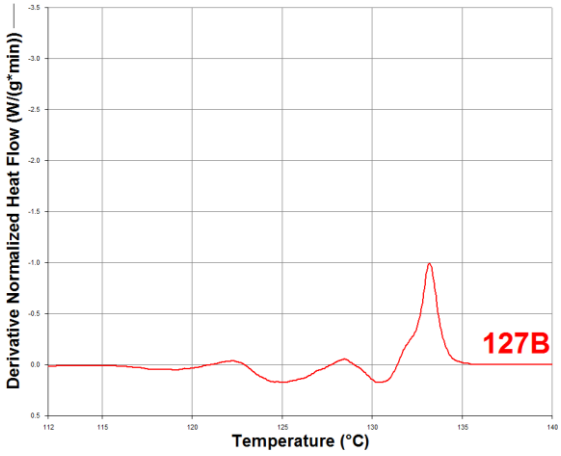


Figure 59. Curve analysis: SIS 1st derivative fingerprint for pipe 127B

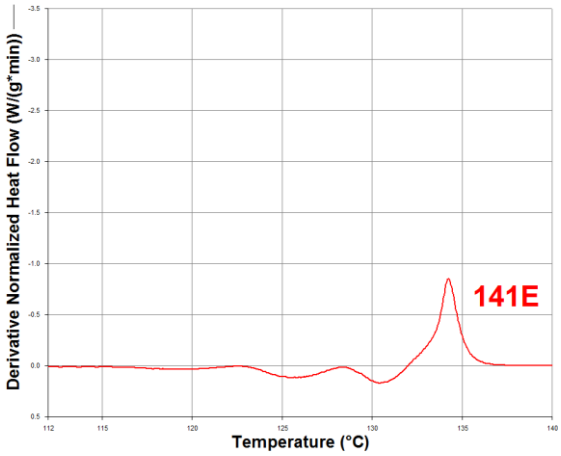


Figure 60. Curve analysis: SIS 1st derivative fingerprint for pipe 141E

3.2 Material degradation assessment

3.2.1 Infrared spectroscopy

A summary of the relevant infrared absorption peaks for polyethylene pipe material is compiled in Table 10. Relevant functional groups of interest in this study were oxidised products or by-products produced during ageing. These included carbonyl, hydroperoxides and several vinyl groups[60].

IR spectroscopy can help the characterisation of carbonyl compounds formed during oxidation processes[61]. Three overlapping components products of thermo and photo oxidation can be recognised by a broad carbonyl stretching band in the IR spectrum. These components are believed to be saturated aldehydes (1733 cm^{-1}), ketones (1721 cm^{-1}) and acids (1712 cm^{-1})[62]. Hydroperoxides are also present in the degradation process as an intermediate and their decomposition is very rapid and cannot be monitored without chemical treatment. In which case, they can be seen at 3555 cm^{-1}. Gedde et al.[63] suggested that the ketonic carbonyl absorption peak is the most prominent of the broad carbonyl band and it can be used to follow oxidative degradation as its formation is fairly constant. Similar researches were conducted by Terselius et al. to conclude that the concentration in carbonyl was a sign of a diffusion-related oxidation process within amorphous regions.

Absorption bands due to hydroxyl species occur in the region 3,600–3,200 cm^{-1}. Unfortunately the carbonyl species which are a consequence of oxidation have fundamental absorption bands that overlap. Because of this discrimination between particular species using the ATR is difficult.

The FTIR of middle surface of the polymer was compared to that of the bore and outside surfaces. The middle part of the pipe wall is taken as reference as it is protected from oxidation. The bore part of the pipe would be less affected by oxidation because of the environment inside the pipe is gas. The outside surface of the pipe is expected to be at an advanced stage of degradation because oxygen is available in great concentration outside of the pipe wall. Figure 61 shows an example of the carbonyl peak absorption at around 1715 cm^{-1}. This is a sign of advanced degradation on the pipe surface. Only a small quantity of pipes showed this.

Table 10. Infrared spectroscopy correlation table[60]

Bond	Type of bond	Specific type of bond	Absorption peak cm^{-1} (nm)	Appearance
C—H	alkyl	Methyl	1260 cm^{-1} (7937 nm)	strong
			1380 cm^{-1} (7246 nm)	weak
			2870 cm^{-1} (3484 nm)	medium to strong
			2960 cm^{-1} (3378 nm)	medium to strong
		Methylene	1470 cm^{-1} (6803 nm)	strong
			2850 cm^{-1} (3509 nm)	medium to strong
			2925 cm^{-1} (3419 nm)	medium to strong
		Methane	2890 cm^{-1} (3460 nm)	weak
	vinyl	$C{=}CH_2$	900 cm^{-1} (11111 nm)	strong
			2975 cm^{-1} (3361 nm)	medium
			3080 cm^{-1} (3247 nm)	medium
		C=CH	3020 cm^{-1} (3311 nm)	medium
		monosubstituted alkenes	900 cm^{-1} (11111 nm)	strong
			990 cm^{-1} (10101 nm)	strong
		cis-disubstituted alkenes	670–700 cm^{-1} (14286-14925 nm)	strong
		trans-disubstituted alkenes	965 cm^{-1} (10363 nm)	strong
		trisubstituted alkenes	800–840 cm^{-1} (11905-12500 nm)	strong to medium
	aromatic	benzene/sub. benzene	3070 cm^{-1} (3257 nm)	weak
		monosubstituted benzene	700–750 cm^{-1} (13333-14286 nm)	strong
			690–710 cm^{-1} (14085-14493 nm)	strong
		ortho-disub. Benzene	750 cm^{-1} (13333 nm)	strong
		meta-disub. Benzene	750–800 cm^{-1} (12500-13333 nm)	strong
			860–900 cm^{-1} (11111-11628 nm)	strong
		para-disub. Benzene	800–860 cm^{-1} (11628-12500 nm)	strong
	alkynes	Any	3300 cm^{-1} (3030 nm)	medium
	aldehydes	Any	2720 cm^{-1} (3676 nm)	medium
			2820 cm^{-1} (3546 nm)	

Bond	Type of bond	Specific type of bond	Absorption peak cm^{-1} (nm)	Appearance
C─C	acyclic C─C	monosub. alkenes	1645 cm^{-1} (6079 nm)	medium
		1,1-disub. alkenes	1655 cm^{-1} (6042 nm)	medium
		cis-1,2-disub. alkenes	1660 cm^{-1} (6024 nm)	medium
		trans-1,2-disub. alkenes	1675 cm^{-1} (5970 nm)	medium
		trisub., tetrasub. alkenes	1670 cm^{-1} (5988 nm)	weak
	conjugated C─C	dienes	1600 cm^{-1} (6250 nm)	strong
			1650 cm^{-1} (6061 nm)	strong
	with benzene ring		1625 cm^{-1} (6154 nm)	strong
	with C═O		1600 cm^{-1} (6250 nm)	strong
	C═C (both sp^2)	any	1640–1680 cm^{-1} (5952-6098 nm)	medium
	aromatic C═C	any	1450 cm^{-1} (6897 nm)	weak to strong (usually 3 or 4)
			1500 cm^{-1} (6667 nm)	
			1580 cm^{-1} (6329 nm)	
			1600 cm^{-1} (6250 nm)	
	C≡C	terminal alkynes	2100–2140 cm^{-1} (4673-4762 nm)	weak
		disubst. alkynes	2190–2260 cm^{-1} (4425-4566 nm)	very weak (often indisinguishable)

Bond	Type of bond	Specific type of bond	Absorption peak cm^{-1} (nm)	Appearance
C=O	aldehyde/ketone	saturated aliph./cyclic 6-membered	1720 cm^{-1} (5814 nm)	
		α,β-unsaturated	1685 cm^{-1} (5935 nm)	
		aromatic ketones	1685 cm^{-1} (5935 nm)	
		cyclic 5-membered	1750 cm^{-1} (5714 nm)	
		cyclic 4-membered	1775 cm^{-1} (5634 nm)	
		Aldehydes	1725 cm^{-1} (5797 nm)	influence of conjugation (as with ketones)
	carboxylic acids/derivates	saturated carboxylic acids	1710 cm^{-1} (5848 nm)	
		unsat./aromatic carb. acids	1680–1690 cm^{-1} (5917-5952 nm)	
		esters and lactones	1735 cm^{-1} (5764 nm)	influenced by conjugation and ring size (as with ketones)
		Anhydrides	1760 cm^{-1} (5682 nm)	
			1820 cm^{-1} (5495 nm)	
		acyl halides	1800 cm^{-1} (5556 nm)	
		Amides	1650 cm^{-1} (6061 nm)	associated amides
		carboxylates (salts)	1550–1610 cm^{-1} (6211-6452 nm)	
		amino acid zwitterions	1550–1610 cm^{-1} (6211-6452 nm)	
O–H	alcohols, phenols	low concentration	3610–3670 cm^{-1} (2725-2770 nm)	
		high concentration	3200–3400 cm^{-1} (2941-3125 nm)	broad
	carboxylic acids	low concentration	3500–3560 cm^{-1} (2809-2857 nm)	
		high concentration	3000 cm^{-1} (3333 nm)	broad

Bond	Type of bond	Specific type of bond	Absorption peak cm^{-1} (nm)	Appearance
C—O	alcohols	Primary	1040–1060 cm^{-1} (9434-9615 nm)	strong, broad
		Secondary	~1100 cm^{-1} (~9091 nm)	strong
		Tertiary	1150–1200 cm^{-1} (8333-8696 nm)	medium
	phenols	Any	1200 cm^{-1} (8333 nm)	
	ethers	Aliphatic	1120 cm^{-1} (8929 nm)	
		Aromatic	1220–1260 cm^{-1} (7937-8197 nm)	
	carboxylic acids	Any	1250–1300 cm^{-1} (7692-8000 nm)	
	esters	Any	1100–1300 cm^{-1} (7692-9091 nm)	two bands (distinct from ketones, which do not possess a C—O bond)

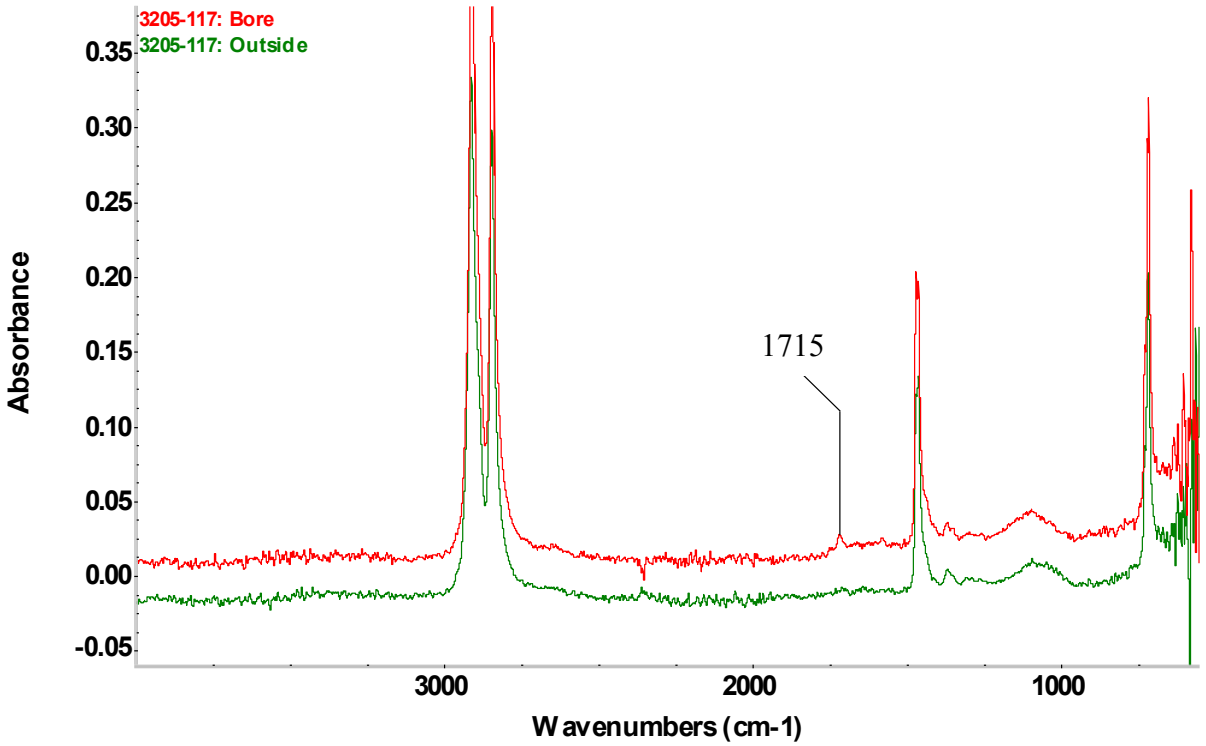


Figure 61. FTIR trace of pipe 3205 117

In Table 11 a summary of the pipes showing advanced degradation is expressed. Carbonyl peaks were detected on the outside surface for the green yellow pipe 1A and 1B. The manufacturing dates for these pipes are unknown. The areas where they were excavated are unknown. Both pipes are made of the second version of the Alathon 5043 resin material. Carbonyl peaks were found on the bore surfaces for other materials. After years in service one would expect that pipes made of the same material and exposed to the same environment would reach the same degradation condition. Here, the metric pipes 127A and 94A are both from area 7 and are both made of the same resin. They are showing the same carbonyl peak at 1720 cm^{-1}. The infrared spectrum may be showing the additive package varying from one pipe to another. However, if this is the case, it would not be expected to only show on the bore for some pipe and outside for others.

Table 11. Pipe samples showing small carbonyl peak on bore and outside surfaces

Exova Code	Colour	Identification	Surface	FTIR peak (cm^{-1})
3205 117A	tan	Alathon 5040	Bore	1720
3205 165A	tan	Alathon 5040	Bore	1720
3 205 187	tan	Alathon 5040	Bore	1715
3205 184D	tan	Alathon 5043 – 2nd version	Bore	1715
3205 1A	green yellow	Alathon 5043 – 2nd version	Outside	1740
3205 1B	green yellow	Alathon 5043 – 2nd version	Outside	1740
3205 094A	green yellow	Alathon 5043 – 2nd version	Bore	1720
3205 163B	green yellow	Alathon 5043 – 2nd version	Bore	1720
3205 127A	bright yellow	MDPE 3	Bore	1720

Following the hypothesis that the FTIR spectra indicate the level of degradation on pipe surfaces, it appears that most of the pipes would be in good condition. The pipes that are showing the carbonyl peaks are mainly showing this on their bore surfaces but not on their outside surfaces. The ability of FTIR to predict end of service life can be discussed when it comes to pipe 117. This pipe has no remaining antioxidants, and therefore is expected to be at an advanced stage of degradation mainly on the outside surface. Here it only shows signs of carbonyl peaks on its bore surface, suggesting that they may potentially belong to additives present in the gas and that they are not due to degradation.

In conclusion it is too early to tell if the pipes are still in good condition using FTIR. OIT however will provide information on the remaining concentration of antioxidant left in the pipes.

3.2.2 Oxidation induction time

A quality assessment was performed on the DSC OIT testing to reveal the variation in the composition of a bright yellow MDPE pipe. The figure was obtained by conducting 16 OIT tests by two different operators on an old gas pipe section. The results acquired suggested little operator and instrument variation with a standard deviation of 2.9 minutes overall. See results below in Table 11.

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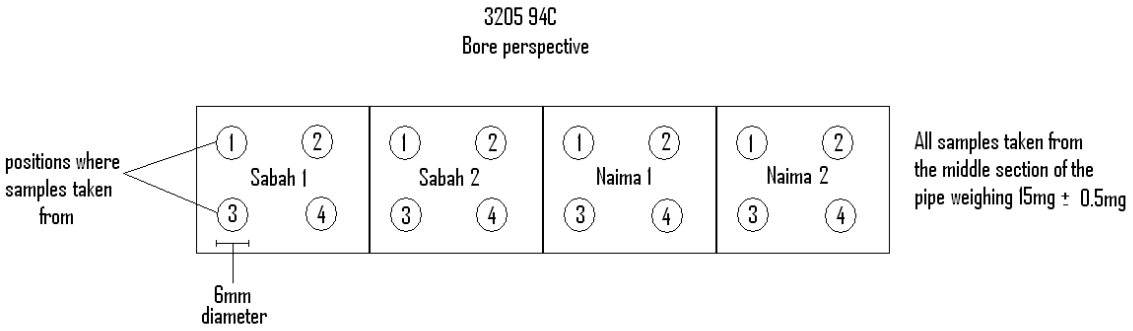


Table 12. OIT-DSC 4000 instrument error

Date tested	Data collected	Diameter is 6mm	Mass (mg)	OIT (min)	Average OIT(min) (operator)	Average OIT(min)	Standard Deviation (operator)	Standard Deviation
02/11/2012	00:57	3205 94C-N1-1	15.5	60.4	58.8	60.0	3.0	2.9
02/11/2012	03:20	3205 94C-N1-2	14.7	58.1				
02/11/2012	05:43	3205 94C-N1-3	15.5	57.9				
02/11/2012	07:45	3205 94C-N1-4	15.5	61.8				
02/11/2012	10:07	3205 94C-N2-1	15.5	59.2				
02/11/2012	11:48	3205 94C-N2-2	15.2	61.9				
02/11/2012	13:27	3205 94C-N2-3	15.4	52.3				
02/11/2012	14:58	3205 94C-N2-4	15.5	58.6				
31/10/2012	13:49	3205 94C-S1-1	15.4	59.2	61.2		2.4	
31/10/2012	15:45	3205 94C-S1-2	15.1	63.6				
01/11/2012	13:45	3205 94C-S1-3	14.8	56.6				
31/10/2012	11:20	3205 94C-S1-4	15.5	63.0				
01/11/2012	15:19	3205 94C-S2-1	15.4	63.0				
01/11/2012	17:48	3205 94C-S2-2	15.1	60.5				
01/11/2012	20:11	3205 94C-S2-3	15.2	60.9				
01/11/2012	22:34	3205 94C-S2-4	14.8	62.4				

3.2.2.1 *Investigation of small exothermic peak in data for tan coloured Aldyl A*

OIT was first conducted on a 15±0.5mg sample disk. The thermograms of the tan samples were showing a small but well-defined exothermic peak before the actual auto-oxidation of the sample. This small peak is shown in Figure 62 was in some cases sharper than the actual oxidation of the sample.

The same effect was noticed by Haydar Jaafar during his research in 1997[64]. Jaafar was studying a medium density PE Aldyl-A 5046, manufactured by DuPont (UK). During his research, he found that the Aldyl A resin showed only one major exothermic peak. However, the Aldyl A pipes which were aged in water for one year at 23°C displayed an additional small but detectable exothermic peak prior to the major exothermic peak. To understand why the premature oxidation peak was happening, he conducted an investigation involving the use of TGA, gel content and FTIR analysis.

The TGA test was conducted with a method similar to the OIT according to the gas

standard PL2/1, (test carried out in oxygen at 200°C until degradation occurred). The TGA experiment showed for the virgin sample that there was approximately a 1% reduction in sample weight up to 25 min. This was attributed to the vaporisation of additives and/or loss of moisture. Thermo-oxidative decomposition happened after 25 minute and was characterised by a weight loss. This weight loss seemed to match the onset of the exotherm in the DSC trace.

The FTIR and Gel-content tests were performed on the melted OIT samples subjected to the 23 min heating period, just before the exothermic reaction started taking place. According to the gel-content results, no cross-linking was found before 23 minutes for the un-aged Aldyl A sample. Evidence for thermal oxidation was not detected via FTIR spectroscopy.

A second series of experiments where the OIT tests were terminated after 25 minutes, just after the start of oxidation were carried out. The gel-content measurement showed evidence that crosslinking had started and the FTIR spectroscopy exhibited an increase in the carbonyl index indicating that thermo-oxidation had taken place.

An Aldyl-A 5046 pipe material aged at 23°C was analysed in a third series of experiment and the OIT tests were terminated after the first exothermic peak was detected at about 30 minutes. The gel-content results showed that approximately 12% of the sample had cross-linked. These specimens did not indicate the presence of oxidation when analysed using FTIR spectroscopy confirming that the first oxidation appearing was not showing degradation within the material but was due to the presence of a cross-linked fraction in the polymer.

In his Research Jaafar demonstrated that the first exothermic peak could be eliminated by terminating the OIT after the first occurrence had taken place and re-starting the OIT testing again. Since no information was available on the additive system used for the Aldyl A resin, it was difficult to give a definitive reason for the observed first peak. However, the evidence suggests that the first peak may be due to the polymer containing a cross-linked fraction.

It was not judged necessary to carry out further research to understand why the first oxidation was happening. Jaafar's work provides one possible explanation, suggesting that the first peak may be due to the polymer containing a cross-linked fraction. Nevertheless, the additives were suspected. This premature oxidation peak was observed for a tan pipe Aldyl A

material and was not seen for green-yellow pipes in this study. The tan colour came from mixing mobyldate orange with the green NBC stabilizer. This UV stabiliser was proved to increase the outdoor life of polyolefins substantially. This stabiliser is unstable in contact with strong oxidising agent such as oxygen and so provides a second explanation for the "bump" seen.

A reason why the peak was not visible for green yellow material during this MSc project (happening almost 15 years after the completion of Jaafar thesis) is that the degradation state of the pipe reduced considerably the OIT value of the material. Therefore the premature oxidation peak is believed to have happened after the actual oxidation of the sample making it impossible to be detected. However this does not explain why the peak is seen within tan samples.

OIT were conducted for the same sample with different masses (5, 10 and 15 mg). The OIT using a 5±0.5mg sample was found to reduce the size of the bump the most. The other advantage of choosing a low sample weight was that it became easy to isolate the bore, outside and middle surface. This was because the sample disks prepared were so thin. Consequently, it was decided to prepare disk samples in this mass range for OIT.

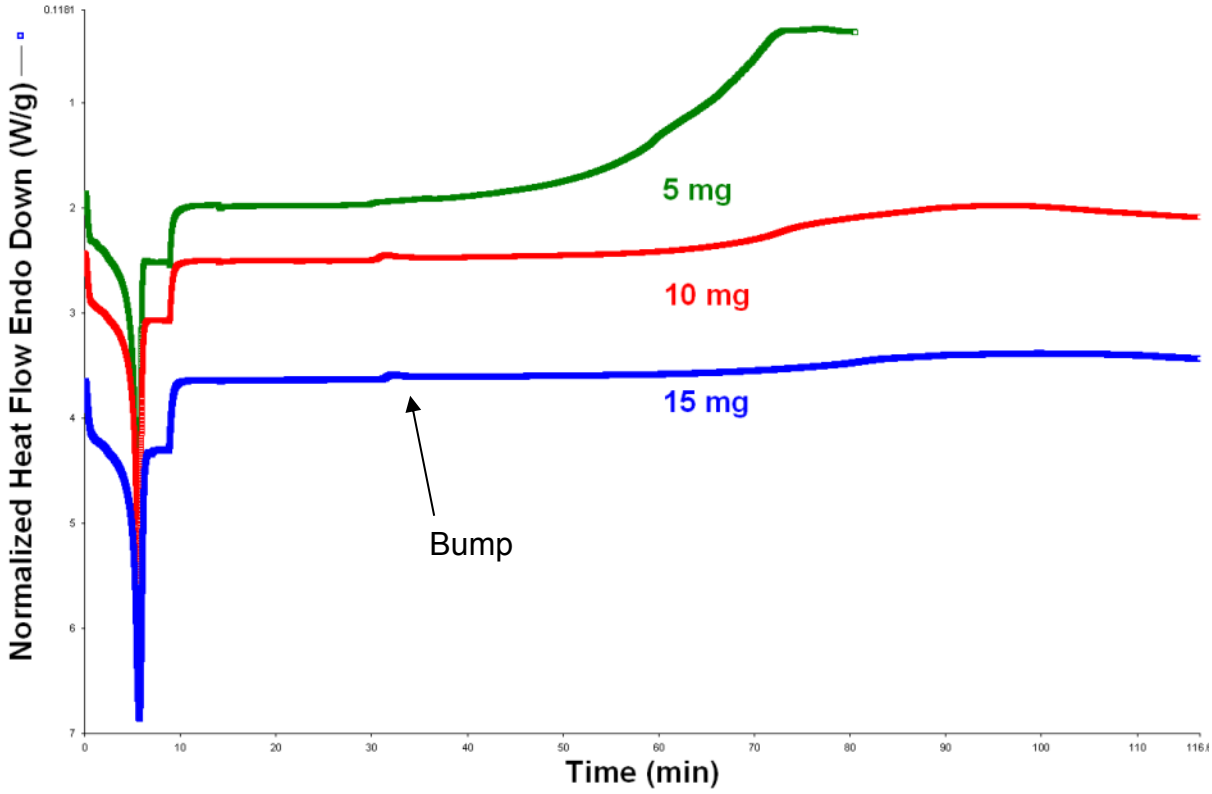


Figure 62. Comparison of OIT thermogram for a pink material (3205 49) with different masses

3.2.2.2 OIT testing for the unexposed material

The OIT requirement for modern PE pipes is over 20 min and therefore PE pipe with OIT close or over 20 min are considered to be well protected against oxidative degradation due to the high amount of antioxidant remaining. The OIT values for the green yellow material vary from 5 to 20 min for all positions (bore, middle and outside).The values are shown in Table 13. The green yellow material can still be considered to have a correct amount of antioxidant for protection against oxidative degradation.

Table 13. OIT values for green yellow materials

Exova Code	Colour	Identification	OIT-B (min)	OIT-M (min)	OIT-O (min)
3205 011	green yellow	Alathon 5046-C	10.6	10.3	4.81
3205 088	green yellow	Alathon 5043 – 2nd version	14.3	16.0	11.4
3205 092A	green yellow	Alathon 5043 – 2nd version	10.7	12.1	13.5
3205 118A	green yellow	Alathon 5043 – 2nd version	12.3	10.4	10.6
3205 118D	green yellow	Alathon 5043 – 2nd version	9.19	10.1	6.14
3205 119A	green yellow	Alathon 5043 – 2nd version	15.6	18.3	11.7
3205 147	green yellow	Alathon 5043 – 2nd version	10.9	15.1	2.40
3205 163B	green yellow	Alathon 5043 – 2nd version	14.8	14.5	13.0
3205 177	green yellow	Alathon 5043 – 2nd version	13.2	3.90	7.30
3205 178J	green yellow	Alathon 5043 – 2nd version	13.1	18.2	10.7

The OIT values are shown in Table 14 for the tan material.

Pipe 117 does not seem to have any antioxidant left in the pipe. While a low OIT on the outside surface could have occurred during service, having a non-existent OIT at the middle and bore surface seems unlikely. It has to be concluded that no antioxidant were added to the pipe when it was manufactured.

Pipe 187 exhibits a very low OIT for the outside surface. It shows a higher OIT value for the bore. Carbonyl peaks were detected on the bore but not on the outside surface for this pipe which as judged by its low OIT was more degraded on the outside than the bore. At this point the FTIR results obtained earlier can be discussed. Carbonyl peaks are the sign that chemical degradation has started happening in the material. The OIT at the middle surface is the highest and the closest to the original OIT of the material. Although this pipe material

was found to be Alathon 5040 it has a different material structure from pipe 117. At this stage it must be considered that there were some manufacturing mistakes made during the production of pipe 117. Perhaps the absence of antioxidant during the processing increased the vulnerability of the pipe toward thermal degradation. And therefore this degradation resulted in a modification of the material leading to the two peaks well segregated by the SIS technique.

Pipe 165 and 188 are meant to be made of the same material as 187, yet they exhibit high divergence in the way their OIT values are evolving. Only pipe 165 and 187 are showing high OIT values at their middle position. The OIT values for the bore and outside surfaces of pipe 165A are almost equal (54.8 and 53.1 minutes respectively). For pipe 188 the OIT value is highest at the outside surface (27.2 minutes) and lowest at the bore (8.8 minutes) leaving a low OIT value for the middle part (22.1 minutes) comparatively to pipe 165A (141 minutes) and pipe 187 (39.7 minutes).

Alathon 5043 materials follow the same OIT pattern as 5040. This means that they appear to be random. When the OIT is the lowest at the bore surface (20.4 min) for 184D, it is strangely high (71.3 min) on the outside. For pipe 169B the OIT is lower at the bore and outside surface (19.8 and 28.9 respectively) than at the middle surface (106 min).

Usually the OIT of the middle part is the highest because it is not as exposed to thermo oxidation as the outside surface or the bore. Tan materials do not follow this trend. This would indicate that the material composition is either really variable or that the antioxidant package given to each pipe is different.

Table 14. OIT values for tan materials

Exova Code	Colour	Identification	OIT-B (min)	OIT-M (min)	OIT-O (min)
3205 068E	tan	Alathon 5043 – 2nd version	140	129	97.4
3205 117	tan	Unique material	<1	<1	<1
3205 165	tan	Alathon 5040	54.8	141	53.1
3205 169B	tan	Alathon 5043 – 2nd version	19.8	106	28.9
3205 184D	tan	Alathon 5043 – 2nd version	20.4	96.5	71.3
3205 187	tan	Alathon 5040	11.5	39.7	3.90
3205 188	tan	Alathon 5040	8.80	22.1	27.2

Compared to the tan material one would say that the pale yellow material (shown in

Table 14) is pretty consistent in terms of OIT, particularly for the middle surface. The OIT at the middle is approximately 25 minutes for 58, 95 and 141E. This is a good sign that the antioxidant depleted in the same way at least at the middle surface of the pipe.

Table 15. OIT values for pale yellow materials

Exova Code	Colour	Identification	OIT-B (min)	OIT-M (min)	OIT-O (min)
3205 058-4	pale yellow	HDPE 1	19.0	23.7	14.4
3205 095	pale yellow	HDPE 1	25.9	25.9	6.77
3205 141E	pale yellow	HDPE 2	7.80	26.6	6.00

Differences in the OIT results between pipes at the bore and outside surface could be due to service location and conditions.

3.2.2.2.1 *Variation in the composition for the tan Aldyl A pipe 68*

The tan Aldyl A materials showing really high OIT values (all greater than 50 minutes) are in Table 16. These high OIT results are rather unusual for 40 year old PE materials. The OIT results are very variable when comparing them from far end sections of 10 meter long pipe. For example they can vary from approximately 54 to 132 minutes on the outside of the tan pipe material between the different sections A1, A3, A4 and A5.

Table 16. Variation in the composition of unexposed pipe 68

3205-68 Unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	116	118	7.5	56.2	0.138
Bore	A1	116				
Bore	A3	108				
Bore	A4	127				
Bore	A5 (mean of three values)	124				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	103	103	17.7	314.2	
Middle	A1	90.8				
Middle	A3	111				
Middle	A4	128.3				
Middle	A5 (mean of three values)	82.9				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	111	91.9	30.5	929.4	0.497
Outside	A1	76.1				
Outside	A3	53.6				
Outside	A4	86.6				
Outside	A5 (mean of three values)	132				

A round robin test revealed that the DSC equipment used for the OIT testing of two modern PE materials was varying by 1 minute. This test program can be used to assess the quality of measurement from the instrument. In this case the DSC instrument used is able to provide accurate results. The results obtained are shown in Table 17.

Table 17. Round robin

Samples	Exova Code	Test Series	Meas. No.	Operator	Date	Mass (mg)	OIT (min)	Standard Deviation	Mean OIT (min)
PE1	POLYM4557	1	1	SR	10/06/2013	7.1	38.4	0.5	37.8
			2	SR	10/06/2013	7.4	36.8		
		2	1	NZ	11/06/2013	7.4	37.7		
			2	NZ	11/06/2013	7.4	37.8		
		3	1	NZ	12/06/2013	7.4	38.0		
			2	NZ	12/06/2013	7.3	37.9		
PE2	POLYM4558	1	1	SR	10/06/2013	7.4	24.2	1.0	24.7
			2	SR	10/06/2013	7.4	25.1		
		2	1	SR	11/06/2013	7.5	23.0		
			2	SR	11/06/2013	7.1	25.6		
		3	1	NZ	12/06/2013	7.2	25.1		
			2	NZ	12/06/2013	7.2	25.2		

Isothermal Oxygen Induction Time (OIT) was carried out in general accordance with ISO11357-6 [1] using Differential Scanning Calorimetry (DSC). The following experimental conditions were used:

Instrument: Heat-Flux Perkin Elmer DSC4000 (Pyris software version 10.1.0.0412)

Sample pan: Open aluminium pan (Perkin-Elmer)

Reference pan: Open aluminium pan (Perkin-Elmer)

Calibration materials: Indium (T_m = 156.6 ± 0.5°C) and tin (T_m = 231.9 ± 0.5°C)

Nitrogen flow rate: 50 cm^3/min (99.998% oxygen-free nitrogen, BOC Industrial UK)

Oxygen flow rate: 50 cm^3/min (oxygen, BOC Industrial UK)

Measurement technique: Tangent method

A yearly calibration of the DSC instrument was carried out with the calibration materials on 11/07/12; monthly calibration checks are also conducted with the calibration materials. The DSC temperature program for PE1 and PE2 are shown in Table 18 and Table 19 respectively. The tests were done as per BS EN ISO 11357-6[65].

Table 18. DSC temperature program for PE1

Start Temperature (°C)	End Temperature (°C)	Heating rate (°C/min)	Isothermal Time (min)	Gas
30	215	20	-	Nitrogen
215		-	5	Nitrogen
215		-	80	Oxygen

Table 19. DSC temperature program for PE2

Start Temperature (°C)	End Temperature (°C)	Heating rate (°C/min)	Isothermal Time (min)	Gas
30	220	20	-	Nitrogen
220		-	5	Nitrogen
220		-	60	Oxygen

Because the variation in the results obtained for the OIT of the tan Aldyl A through the thickness of the pipe at different locations is so large it is suspected that the material composition is inconsistent throughout.

The standard deviation is surprisingly greater at the middle part of the pipe (approximately 18 minutes) than at the bore part (approximately 8 minutes). The middle part of the pipe wall is expected to be the most stable in term of OIT value since the bore and outside part can act as protective barriers toward the oxidative attacks coming from the oxygen molecule. In other words, the OIT of the middle part is the closest to the original OIT of the pipe material.

There are great chances that such OIT variations are due to the master-batching process. The master-batching process could have brought inconsistency to the pipe composition by creating pockets with high concentration of antioxidants whilst leaving some positions unprotected within the pipe.

The OIT variation is even greater on the outside surface of the tan pipe with a standard deviation of approximately 31 minutes. Although a lower overall OIT is expected on the outside of the pipe it is not expected that it varies so significantly. This phenomenon nonetheless supports the hypothesis that the masterbatching is playing a leading role in the unpredictable OIT results. The oxidative reactions would reduce the OIT considerably in places where the antioxidant concentration would be lower.

The average OIT of the bore part (118 min) tends to be slightly higher than the average OIT at middle part (103 min). As explained earlier, the OIT of the middle part is usually the closest to the original OIT of the material and is expected to have the highest OIT value. This is not the case here.

Student's t-tests were conducted to give information about trends within the OIT data. A t-test is any statistical hypothesis test in which the test statistic follows a student's t distribution if the null hypothesis is supported. It can be used to determine if two sets of data are significantly different from each other.

The OIT values of the bore and outside surfaces were compared to the middle surface. The student's t-tests was used to find out if the mean OIT values of the bore or outside and the mean OIT values of the middle were statistically different from each other. For this, a two-tailed distribution with unequal variance was the chosen with a 95% confidence limit. The null-hypothesis was that there was no significant difference between the mean OIT value of the bore or outside and the mean OIT value of the middle part. The probability that the results observed are due to chance becomes high if the p value is higher than 0.05. There will be no significant difference between two values at the 5 per cent chance or 0.05 significance level if the p value is higher than 0.05. For a p value lower than 0.05, there will be a significant difference between two values at a 5 per cent chance or 0.05 significance level.

This test showed there was no significant difference between the mean OIT of the bore and mean OIT of the middle part for the tan pipe at the 5 per cent chance or 0.05 significance level ($p=0.138>0.05$). The same conclusion was reached when comparing the mean OIT of the outside parts against the middle ($p=0.497>0.05$).

The fact that the student's t-test assigns the difference in value to chance confirms that the material is variable within its composition. The student's t-test can help assessing the variability of a material before conducting further work. It is expected that the OIT of this

material after exposure will be unpredictable. This can seriously affect the ability to predict remaining lifetime which is based on oxidation induction time for exposed materials.

3.2.2.2.2 *Variation in the composition for the green yellow Aldyl A pipe 57*

The OIT values for the green yellow Aldyl A pipe 57 vary between 10 and 20 minutes for different sections of the 10 meter long pipe as shown in Table 20. The OIT results are relatively good on average for an old PE pipe as modern PE only have an OIT requirement of more than 20 minutes. Again, the standard deviation is increasing going from a low 0.9 minute value for the bore part of the pipe to a 2.6 minute on the outside part of the pipe. The crystalline content may have been slightly lower on the outside surface than the bore where slower cooling would have led to a smaller number of large spherulites and a slightly higher crystalline content which may have indirectly affected the OIT value. It is worth nothing that oxygen molecules usually start the oxidation reactions in the most amorphous part of the polymer. In this case, the outside part of the pipe would be the most amorphous. However we can conclude that the green yellow material is much less variable than the tan material 68 although the SIS results are showing that they were made from the same resin material.

Table 20. Variation in the composition of unexposed pipe 57

3205-57 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	19.3	18.4	0.9	0.7	0.082
Bore	C	17.5				
Bore	D	17.8				
Bore	F	18.9				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	16.3	15.9	2.0	4.1	
Middle	C	16.8				
Middle	D	17.4				
Middle	F	12.9				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	15.2	11.3	2.6	6.8	0.036
Outside	C	9.70				
Outside	D	10.5				
Outside	F	9.90				

The student's t-test revealed that there was no significant difference between the mean

OIT of the bore and mean OIT of the middle part for the green yellow pipe at the 5 per cent or 0.05 significance level ($p=0.082>0.05$). However, the conclusion reached for the outside part of the pipe compared to the middle was different. The student's t-test revealed that there was a significant difference between the mean OIT of the outside and the mean OIT of the middle part for the tan pipe at the 5 per cent or 0.05 significance level ($p=0.036<0.05$). Knowing that pipe 57 was a 2 inches green yellow pipe supposed to be the same material as the tan pipe except in colour, it is possible that it may have been subjected to slightly different processing methods as it was processed in the UK. This material was not expected to be variable on the outside surface however it was shown in the identification work that it was made of the same material as pipe 68 which is variable on all surfaces. The OIT data will be examined with care when conducting the exposure work for pipe 57 as the results may be variable on the outside as well as the bore surface.

3.2.2.2.3 *Variation in the composition for the green yellow Aldyl A pipe 36*

For the same formulation as pipe 57, the green yellow Aldyl A pipe 36 shows OITs values varying from between approximately 6 and 16 minutes for different sections of the 10 meter long pipe. This is shown in Table 21.

Table 21. Variation in the composition of unexposed pipe 36

3205-36 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	8.82	9.5	0.7	0.5	0.854
Bore	7A	9.20				
Bore	8	10.4				
Bore	JC	10.1				
Bore	4	9.09				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	6.84	9.3	1.8	3.3	
Middle	7A	9.91				
Middle	8	11.8				
Middle	JC	9.35				
Middle	4	8.68				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	11.9	12.6	2.8	7.7	0.061
Outside	7A	15.5				
Outside	8	15.6				
Outside	JC	9.67				
Outside	4	10.5				

Pipe 36 is thicker than pipe 57. As a result the bore surface of pipe 36 would take relatively longer to cool down leading to an increase in larger more prefect spherulites. Therefore the bore part of pipe 36 would be expected to be more crystalline than pipe 57. Slower cooling would also result in greater consumption of antioxidants and hence a shorter OIT

The standard deviation for this pipe follows the same trend as the previous two pipes. The standard deviation rises from 0.7 minutes at the bore surface to 2.8 minutes on the outside of the pipe. The quench cooling, leading to the formation of a large number of small imperfect spherulites per unit volume on the exterior surface of the pipe, may have indirectly affected the OIT value. At this point it is difficult to tell if the difference between the standard deviation at the bore part for pipe 36 (0.7 minutes) is significantly different from the standard deviation at the bore part for pipe 57 (0.9 minutes). However the fact that the standard deviation for pipe 36 is lower than the standard deviation for pipe 57 supports the belief that the bore part of pipe 36 is more consistent because it has higher crystalline content.

The mean OIT of the bore is the same as the mean OIT of the middle (9.5 minutes and 9.3 minutes respectively). The mean OIT of the outside has the highest value (12.6 minutes). This surface is also the most variable surface in terms of OIT. It is unclear why the OIT is higher on the outside surface where it is expected to be lowest. Since the formulation is unknown one can only suspect that the antioxidant package in pipe 57 is different from the one in pipe 36.

The student's t-test revealed that there was no significant difference between the mean OIT of the bore and mean OIT of the middle part for the green yellow pipe at the 5 per cent or 0.05 significance level ($p=0.854>0.05$). For the outside surface of the pipe compared to the middle the conclusion reached was different than for pipe 57. The student's t-test revealed that there was no significant difference between the mean OIT of the outside and the mean OIT of the middle part for the green yellow pipe at the 5 per cent or 0.05 significance level ($p=0.061>0.05$). This material is expected to be variable on the outside surface and this may be an issue when conducting the exposure work.

3.2.2.2.4 *Variation in the composition for the pale yellow HDPE pipe 58*

Pipe 58 is a pale yellow, HDPE pipe material. The OIT values vary from 5 to 24

minutes as seen in Table 22. Here the expected OIT trend is observed. The mean OIT of the middle (23.3 minutes) is higher than the bore (19.0 minutes) and the outside (12.2 minutes). The mean OIT for the outside is the lowest because it was the most subject to oxidation. Although, the standard deviation stays about the same on the middle and bore surface of the pipe (1.7 and 1.5 minutes respectively) it is not unsurprising as these values are reasonably low. It was expected to find the lowest standard deviation for the middle surface because it is the least exposed to oxygen. The standard deviation for the outside is around 4.7 min. It was anticipated that the standard deviation on the outside would show the highest variation since oxygen is abundant on the external wall of the pipe in service.

Table 22. Variation in the composition of unexposed pipe 58

3205-58 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	20.9	19.0	1.5	2.1	0.003
Bore	C	18.7				
Bore	3	19.7				
Bore	4	19.0				
Bore	5	16.9				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	23.6	23.3	1.7	2.7	
Middle	C	24.6				
Middle	3	24.1				
Middle	4	23.7				
Middle	5	20.4				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	16.6	12.2	4.7	22.1	0.004
Outside	C	15.3				
Outside	3 (mean of two values)	5.30				
Outside	4	14.2				
Outside	5	9.41				

The student's t test revealed that both mean OIT for the outside ($p=0.004<0.05$) and bore ($p=0.003<0.05$) surfaces of the material were significantly different to the mean OIT of the middle part. Therefore one can predict that the HDPE pipe will not be as variable as the other types of Aldyl A and trends will be more visible when conducting the exposure work.

3.2.2.2.5 *Variation in the composition for the tan Aldyl A pipe 117*

Pipe 117 is a 4 inches diameter, tan Aldyl A pipe. Carbonyl functions were detected

on the internal surface of this pipe via FTIR. Carbonyl groups are often an indicative of polymer degradation. Polymer degradation starts when there is no antioxidant left in the material. The oxygen molecules start attacking the polymer resulting into chain scission and carbonyl formation. Earlier, it was suggested that the material might not have had any antioxidant to begin with and this would explain why the OIT result for this material through the pipe wall are below 1 min. The OIT results for the unexposed tan pipe 117 can be found in Table 23.

Table 23. Variation in the composition of unexposed pipe 117

3205-117 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	A	0.550	0.620	0.1	0.0	0.039
Bore	C	0.770				
Bore	D	0.540				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	A	0.250	0.260	0.0	0.0	
Middle	C	0.250				
Middle	D	0.280				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	A	0.420	0.673	0.4	0.2	0.238
Outside	C	1.17				
Outside	D	0.430				

As the OIT of the material was reduced in the same mode throughout the pipe one could suggest that this material will not be as variable as the tan 68 pipe. However, the student's t test revealed that the mean OIT of the bore surface of the material was significantly different to the mean OIT of the middle surface ($p=0.039<0.05$). The inverse conclusion was reached when comparing the outside and middle surface ($p=0.238>0.05$) of the same pipe. Earlier this phenomenon was attributed to the processing route chosen during which the quench cooling on the outside which may have been brutal. This material is expected to be variable on the outside surface and this may be an issue when conducting the exposure work.

3.2.2.2.6 *Variation in the composition for the green yellow Aldyl A pipe 66*

The OIT results for the unexposed green yellow pipe 66 can be found in Table 24. The mean OIT seems to be consistent through the pipe with approximately 10 minutes on the bore, middle and outside surfaces of the pipe. The standard deviation follows the same trend as for pipe 58. The values are very similar for the bore and middle surfaces (0.3 and 0.5 minutes respectively). The standard deviation is the highest as expected on the outside surface (2.7 minutes).

Table 24. Variation in the composition of unexposed pipe 66

3205-66 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	10.5	10.2	0.3	0.1	0.234
Bore	A END	9.99				
Bore	B END	10.1				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	9.75	9.73	0.5	0.2	
Middle	A END	9.24				
Middle	B END	10.2				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	7.25	9.94	2.7	7.4	0.908
Outside	A END	9.86				
Outside	B END	12.7				

The student's t-test revealed that there was no significant difference between the mean OIT of the bore and mean OIT of the middle part for the tan pipe at the 5 per cent or 0.05 significance level ($p=0.234>0.05$). The conclusion reached was the same on the outside of the pipe ($p=0.908>0.05$), however, this material is still expected to be variable on the outside surface.

Three more green yellow pipes were suggested for an extension of the exposure work. They were made of the same material than pipe 36 but with different pipe diameters. One would expect these pipes to follow the same trends as pipe 36.

3.2.2.2.7 *Variation in the composition for the green yellow Aldyl A pipe 150*

The OIT results for the unexposed green yellow pipe 150 can be found in Table 24.

The mean OIT values for this pipe are between 8.50 and 13.1 min.

Table 25. Variation in the composition of unexposed pipe 150

3205-150 unexposed						
Position	Section code	OIT Bore	Mean	standard deviation	Variance	T test
Bore	Random	12.3	13.1	1.4	1.9	0.136
Bore	2A	12.3				
Bore	5A	14.7				
Position	Section code	OIT Middle	Mean	standard deviation	Variance	
Middle	Random	11.7	10.4	2.0	4.1	
Middle	2A	8.07				
Middle	5A	11.4				
Position	Section code	OIT Outside	Mean	standard deviation	Variance	T test
Outside	Random	5.80	8.53	3.1	9.6	0.440
Outside	2A	7.89				
Outside	5A	11.9				

The standard deviation evolution is the same as for pipe 36. The standard deviation is low for the bore (1.4 minutes) and high for the outside (3.1 minutes) compared to the middle surface (2.0 minutes). This correlates with the hypothesis that the quench cooling leading to the formation of a large number of small imperfect spherulites per unit volume on the exterior surface of the pipe and a slightly lower crystalline content may have indirectly affected the OIT values. It is difficult to explain why the bore has a lower standard deviation than the middle, but this difference may not be significant.

The student's t test shows that there was no significant difference between the mean OIT of the outside ($p=0.440>0.05$) and the mean OIT of the middle part for the green yellow pipe at the 5 per cent or 0.05 significance level. The same conclusion was reached when comparing the mean OIT of the bore and the mean OIT of the middle.

To summarise pipe 150 has the same behaviour as pipe 36, therefore the outside surface of this pipe is expected to be variable in term of OIT.

As a result pipes 119 and 161, made of the same material as pipe 36 and 150, are expected to be variable in term of OIT values which will affect analysis of results from

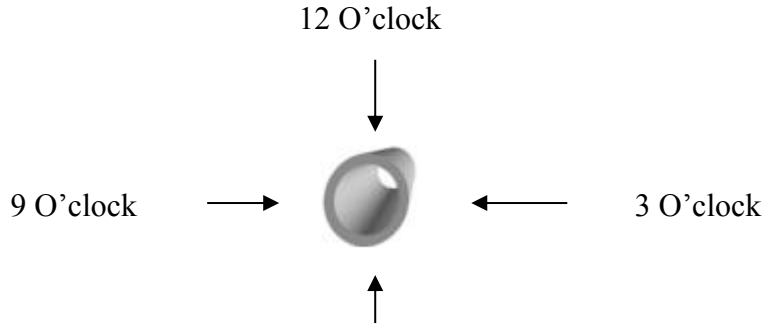
exposure work.

Pipe 165 is a tan Aldyl A material. The SIS thermogram showed that its material structure was different to the tan pipes 68 and 117. Therefore, it is not expected for pipe 165 to present the same behaviour as the tan pipes analysed in this section.

3.2.2.3 Variation around the circumference

After analysing the OIT data along the pipes length it became clear that most of the pipes (except for the pale yellow HDPE 58 and the green yellow pipe 57) were significantly variable in the longitudinal direction. It was then important to make sure that the OIT was not also variable around the circumference of the pipe. Two pipes were chosen for this work; pipe 68 because of its high OIT variability and pipe 36 which seemed to be less variable but still inconsistent throughout the pipe length. These pipes could also be found in larger quantity than other.

The OIT was taken around the pipe's circumference at four equidistant positions and through the pipe thickness, as shown below. Different sections of these pipes were also analysed in order to understand how the OIT around the circumference would vary along the pipe length. Some sections were chosen as a reference when the top position of the pipe in the ground was known or almost certain. The idea behind this was to make sure that the OIT were not affected by the position of the pipe in the ground. In service the bottom part of the pipe (6 o'clock position) is exposed to damper conditions than the top part of the pipe (12 o'clock position), therefore one could expect the OIT value at the top outside surface to be higher than the bottom outside surface. This is because water extracts antioxidants more easily than air. The OIT on the side of the pipe (3 and 9 o'clock position) would be expected to be between the OIT results of the top and bottom part of the pipe circumference.



6 O'clock

The OIT results for a position on the pipe were taken out of the same punch/cylinder for the bore, outside and middle surfaces. This was meant to reduce the variability in the composition of the pipe.

Pipe 68 top position in the ground was clearly defined at its arrival to the laboratory for one of its sections. Therefore, section E was identified as the reference and its top position was called the 12 o'clock position. The 3, 6 and 9 o'clock positions were taken on the pipe circumference at 90 degrees away from each other and following a clockwise motion. The positions were randomly taken for section 1 and 5 of pipe 68 A still following a clockwise motion at 90 degree away from each other. The OIT results for pipe 68 are summarised in Table 26, Table 27 and Table 28.

Table 26. Variation in the composition of unexposed pipe 68E circumference

68 E						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	119	122	5.5	30.0	0.442
6		128				
9		125				
12 (True top)		116				
3	Middle	130	117	9.9	98.3	
6		118				
9		115				
12 (True top)		106				
3	Outside	73.5	81.2	18.1	328.5	0.020
6		89.0				
9		102				
12 (True top)		60.4				

Table 27. Variation in the composition of unexposed pipe 68 A1 circumference

68 A1						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	140	126	19.1	364.6	0.045
6		126				
9		99.5				
12 (Random top)		140				
3	Middle	105	96.5	7.8	60.7	
6		86.2				
9		98.4				
12 (Random top)		96.3				
3	Outside	78.3	84.2	11.4	129.9	0.133
6		90.1				
9		96.9				
12 (Random top)		71.6				

Table 28. Variation in the composition of unexposed pipe 68 A5 circumference

68 A5						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	133	132	4.5	20.7	0.151
6		128				
9		129				
12 (Random top)		138				
3	Middle	102	119	13.9	192.3	
6		135				
9		123				
12 (Random top)		115				
3	Outside	75.8	81.2	10.3	106.2	0.006
6		91.4				
9		69.4				
12 (Random top)		88.0				

3.2.2.3.1 *Variation around the circumference for the tan Aldyl A pipe 68 E*

The standard deviation is the lowest (5.5 minutes) for the bore surface around the circumference of pipe 68 E. The highest value is obtained for the outside around the circumference (18.1 minutes). The standard deviation for the middle around the circumference reaches 9.9 minutes. These values are really high compared to the standard deviation obtained for the round robin test (0.5 - 1 min) for modern gas pipes. As well as been variable along the pipe length the OIT is variable all the way around the pipe circumference of the reference section. Unexpectedly the OIT is not following a pattern when comparing the same surfaces. For example, from the outside point of view, the OIT at the top position of the pipe is actually lower (60.4 minutes) then at the bottom of the pipe. This does not make sense if one wants to find a correlation between the position of the pipe in the ground and the reason for the variability within the OIT results. As the top surface of the pipe is exposed to dryer conditions than the bottom of the pipe, the OIT is expected to be higher at the top because less antioxidants are extracted in dryer soils.

The student's t test revealed that the OITs from the outside of the pipe are statistically the same as those from the middle of the pipe ($p=0.020<0.05$). But this is not the case for the bore compared with the middle part of the pipe ($p=0.442<0.05$). In conclusion pipe 68 has variable material structure through its length and circumference.

3.2.2.3.2 *Variation around the circumference for the tan Aldyl A pipes 68 A1 and A5*

Position 1 and 5 are at the extremities of pipe 68 A. It has already been demonstrated with the pipe reference 68 E that the material, as well as been variable through the length, is also really variable around the circumference. The same conclusion would be expected for sections A1 and A5. First, bearing in mind a very high standard deviation for both sections, the values are 19.1 minutes (bore), 7.8 minutes (middle), and 11.4 minutes (outside) for 68 A1 and 4.5 minutes (bore), 13.9 minutes (middle) and 10.3 minutes for 68 A5 (outside). The pipe is showing variable OITs around the circumference at its far end positions. The standard deviation is not always the lowest for the bore, so there are positions within the pipe showing even more variation then others through the pipe length. This variability in the data shows that the OIT results for the tan material are unpredictable around the circumference of the 2 inch diameter pipe as well as through the length of the pipe.

The mean OIT of the bore, the middle and the outside surface when comparing 68 A1,

A5 and E is effectively the same taking account of it being such a variable material. The mean OIT range for the bore is 122 to 132 minutes. The mean OIT range for the middle is 97 to 117 minutes and the mean OIT range for the outside is 81 to 84 minutes. However, when comparing the OIT values individually the range becomes larger. The OIT range for the individual values for the bore surface on the three sections is from approximately 100 to 140 minutes. For the middle it is from approximately 86 to 135 minutes and from approximately 60 to 97 minutes for the outside. This material is definitely variable, and this could be a problem for the ageing work as the sample is taken randomly from the circumference of a half pipe.

The student's T test shows that the OIT values for the bore and middle parts of pipe 68 A1 are close ($p=0.045<0.05$) however the outside and middle parts are very different in term of OIT values ($p=0.133>0.05$).

As A1 and A5 section are part of the same pipe and therefore share the same composition, it can be concluded that the pipe processing, more particularly, the way that the pipe was quench cooled on the outside, was not consistent along the length of the pipe.

3.2.2.3.3 *Variation around the circumference for the green yellow Aldyl A pipe 36*

The same work was conducted on the green yellow pipe 36 which was less variable regarding to the OIT results comparatively to the tan pipe 68. One of the pipe sections (7C) was showing a small longitudinal crack. This crack was later attributed to a damage possibly caused by a crane attempting to dig up the pipe off the ground. This supposition led to think that the crack position might also refer to the top position of the pipe. For this reason the crack position was identified as the 12 O'clock position while the 3, 6 and 9 O'clock positions were taken on the 36 7C pipe circumference at 90 degrees away from each other following a clockwise motion. The positions were randomly taken for section 1C and 2C of pipe 36 at 90 degrees away from each other and still following a clockwise motion. The OIT results for pipe 36 are summarised in Table 29, Table 30 and Table 31.

Table 29. Variation in the composition of unexposed pipe 36 7C circumference

36 7C						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	9.62	9.57	0.2	0.1	0.002
6		9.38				
9		9.40				
12 (Crack)		9.88				
3	Middle	10.5	10.4	0.2	0.0	
6		10.6				
9		10.1				
12 (Crack)		10.3				
3	Outside	12.9	12.5	0.7	0.5	0.005
6		12.3				
9		11.6				
12 (Crack)		13.1				

Table 30. Variation in the composition of unexposed pipe 36 1C circumference

36 1C						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	20.9	20.8	0.3	0.1	0.000
6		21.1				
9		20.6				
12 (random top)		20.5				
3	Middle	13.8	14.0	0.4	0.2	
6		14.0				
9		13.6				
12 (random top)		14.6				
3	Outside	14.2	13.4	3.5	1.0	0.340
6		13.8				
9		13.7				
12 (random top)		11.9				

Table 31. Variation in the composition of unexposed pipe 36 2C circumference

36 2C						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	9.77	9.56	0.3	0.1	0.000
6		9.06				
9		9.72				
12 (random top)		9.70				
3	Middle	8.38	7.93	0.3	0.1	
6		7.83				
9		7.69				
12 (random top)		7.83				
3	Outside	10.1	9.98	0.4	0.1	0.000
6		10.4				
9		9.54				
12 (random top)		9.87				

3.2.2.3.4 *Variation around the circumference for the green yellow Aldyl A pipes 36-7C 1, 2 and 3*

The standard deviation obtained for the bore, middle and outside surface are low (0.2, 0.2 and 0.7 minutes respectively). The OIT results are very close together for each surface analysed therefore it can be anticipated that the OIT results will be pretty stable around the circumference for the rest of the pipe. Again the theory that the pipe position in the ground is affecting the OIT is not verified here. The 12 o'clock position has the highest OIT value on the outside (13.1 minutes) but the 6 o'clock position (12.3 minutes) does not reach the expected lowest OIT value.

The student's t test shows that both the bore ($p=0.002<0.05$) and the outside ($p=0.003<0.05$) surfaces of the pipe are similar to the middle surface around the circumference. If the pipe is less variable around the circumference it is important to take the sample for the ageing work from the same pipe section along its length and the level of this variability must be checked. This work was conducted at two nearby circumferences.

One circumference (36 7C-1) was chosen for reference and a second circumference (36 7C-2) was taken on the same plan but 1 cm away (in a clockwise motion) from the reference OIT samples. The third circumference (36 7C-3) was taken in a parallel plan 10 cm

away from where samples for 36 7C-1 were taken. The data is summarised in Table 32, Table 33 and Table 34.

Table 32. Variation in the composition of unexposed pipe 36 7C-1 circumference

36 7C-1						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	9.62	9.57	0.2	0.1	0.002
6		9.38				
9		9.40				
12 (Crack)		9.88				
3	Middle	10.5	10.4	0.2	0.0	
6		10.6				
9		10.1				
12 (Crack)		10.3				
3	Outside	12.9	12.5	0.7	0.5	0.005
6		12.3				
9		11.6				
12 (Crack)		13.1				

Table 33. Variation in the composition of unexposed pipe 36 7C-2 circumference

36 7C-2						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	8.83	9.02	0.2	0.1	0.004
6		9.08				
9		9.34				
12 (Crack)		8.81				
3	Middle	11.2	10.6	0.5	0.3	
6		10.7				
9		9.93				
12 (Crack)		10.7				
3	Outside	12.7	13.3	1.2	1.5	0.017
6		15.0				
9		12.2				
12 (Crack)		13.1				

Table 34. Variation in the composition of unexposed pipe 36 7C-3 circumference

36 7C-3						
Position	Surface	OIT	Mean	Standard Deviation	Variance	T test
3	Bore	9.03	9.12	0.1	0.0	0.004
6		9.09				
9		9.20				
12 (Crack)		9.15				
3	Middle	10.3	10.6	0.4	0.1	
6		10.7				
9		11.1				
12 (Crack)		10.3				
3	Outside	13.3	11.9	0.9	0.9	0.065
6		11.2				
9		11.6				
12 (Crack)		11.5				

The standard deviation values for the second position (7C-2) for the bore (0.2 minutes), middle (0.5 minutes) and outside (1.2 minutes) are low. As are the standards deviation values for the bore (0.1 minutes), middle (0.4 minutes) and outside (0.9 minutes)

surfaces of the third position (7C-3). The mean OIT results follow the same trend for 7C-2 as the reference position 7C-1 for which the bore has a lower value than the middle (9.57 and 10.4 minutes respectively) with a higher outside OIT value (12.5 minutes). The mean OIT for 7C-3 also follows the same trend (9.12 minutes for the bore, 10.6 for the middle and 11.9 minutes for the outside) however the mean OIT for the outside is lower.

The student's t test shows that the bore ($p=0.004<0.05$) and outside ($p=0.017<0.05$) surface of 7C-2 are similar to the middle. This is also the case for the bore ($p=0.004<0.05$) surface for 7C-3 that is 10 cm away. The outside ($p=0.065>0.05$) however is different from the middle. In conclusion although the OIT is stable around the circumference of the green yellow pipe the values can change drastically one centimetre further along the pipe. This pipe composition is uneven, making analysis of thermal degradation testing difficult.

3.2.2.3.5 *Variation around the circumference for the green yellow Aldyl A pipes 36 1C and 2C*

The standard deviation values obtained for the bore, middle and outside of the pipe in section 2C are low (values around 0.3 minutes) however, for the pipe section 1C the standard deviation is relatively high on the outside circumference comparatively to the reference (0.7 minutes). The mean OIT results do not follow any particular trend unlike previously when 3 close circumference plans were compared. For pipe section 1C the mean OIT is higher for the bore (20.8 minutes), then comes the mean OIT of the middle (14.0 minutes) and the lowest value is reached for the mean OIT of the outside (13.4 minutes). The mean OIT of the bore and the outside are around 10 minutes for section 2C when the mean OIT of the outside reaches 7.93 minutes. There is no correlation between the two trends and they are both different from the mean OIT trend of the reference section 7C-1. Also, the mean OIT of the bore for pipe 36 1C is very high (20.8 minutes) comparatively to section 7C and 2C (for which the OIT is around 10 minutes). The OIT results for section 1C are generally much higher than for sections 2C and 7C. Knowing that all these sections came from the same 10 meter long pipe it can be concluded that any section of pipe 36 section chosen for the ageing work will show variable OIT results.

3.2.2.3.6 *Variation in the composition for the exposed pipe material*

In order to understand the variability of the OIT results in the exposure work, it was

proposed to repeat some of the OIT testing. Repeats were carried out by two different operators using the same sampling conditions and method as in the exposure work. The testing was conducted on 3 green yellow and 1 tan pipes.

The tan pipe chosen was pipe 68, and previous work on the unexposed pipe already proved that this pipe is variable in terms of OIT. The standard deviation reached for this pipe after 5400 hours of exposure was high for the outside surface (10.6 minutes). This was expected since the unexposed material is variable. The student's t-test suggested that was no significant difference between the mean OIT obtained from both operators at the 5 per cents chance or 0.05 significance level ($p=0.691>0.05$). It is also interesting to see that nothing had happened to the tan pipe even after 5400 hours of ageing at 90^0C. The mean OIT value from both operators is still very high (58.0 ± 10.6 min). Results can be found in Table 35.

Table 35. Variation in the composition of exposed pipe 68

Datafile	OIT (min)	Average OIT(min) (operator)	Variance	Average OIT(min)	Standard Deviation (operator)	Standard Deviation	T test
68-O@90 5400H VCC-JBT-1	69.4	56.3	171.8	58.0	13.1	10.6	0.691
68-O@90 5400H VCC-JBT-2	40.0						
68-O@90 5400H VCC-JBT-3	51.8						
68-O@90 5400H VCC-JBT-4	63.9						
68-O@90 5400H VCC-NZ-1	49.9	59.6	83.9		9.2		
68-O@90 5400H VCC-NZ-2	55.3						
68-O@90 5400H VCC-NZ-3	71.1						
68-O@90 5400H VCC-NZ-4	62.2						

Meaning of 68-O@90 5400H VCC-JBT-1

Pipe code: 68

Surface tested: O means outside

Exposure temperature: @90 means at 90°C

Duration of exposition: 5400H

Type of testing: VCC means Variation composition check

Operator: JBT

Repeat number: 1

The green yellow pipe 57 showed a standard deviation of 5.2 minutes. It must be assumed that this pipe material is also variable in terms of OIT. Again, and this is not a surprise, the tudent's t-test result for this pipe was higher than 0.005, which would mean that there is no operator dependency. Also, it must be concluded that the ageing work did not affect the OIT at all. The mean OIT for both operators for the outside surface of the exposed pipe after 5400 hours of testing was still quiet high (16.9 minutes). Results can be found in Table 36.

Table 36. Variation in the composition of exposed pipe 57

Datafile	OIT (min)	Average OIT(min) (operator)	Variance	Average OIT(min)	Standard Deviation (operator)	Standard Deviation	T test
57-O@90 5400H VCC-JBT-1	13.5	20.1	33.6	16.9	5.8	5.2	0.116
57-O@90 5400H VCC-JBT-2	27.4						
57-O@90 5400H VCC-JBT-3	21.0						
57-O@90 5400H VCC-JBT-4	18.3						
57-O@90 5400H VCC-NZ-1	15.0	13.8	2.4		1.6		
57-O@90 5400H VCC-NZ-2	12.1						
57-O@90 5400H VCC-NZ-3	15.2						
57-O@90 5400H VCC-NZ-4	12.8						

Pipe 36 is a green yellow pipe that was confirmed to be not as variable as tan samples but more variable than the HDPE sample. This again was verified during the exposure work. The standard deviation reached for the samples after 5400 hours of exposure was 1.5 minutes between the two operators. However the student's t-test revealed a trend between the two operators. The OIT results for JBT were generally lower (OIT mean of 8.5 minutes) than the OIT results for NZ (OIT mean of 11.1 minutes). To understand if the choice of the operator had an effect on the OIT results it was decided to have NZ repeating JBT tests. The mean value obtained by NZ was then 9.2 minutes with a bigger standard deviation value (1.6 instead of 0.1 min). It seemed that the variation in the composition of the pipe 36 on the outside was causing the variation within the OIT results. In conclusion the OIT values obtained were not dependent on the operator carrying out the testing but have high standard deviations due to the variability within the pipe's composition. The same work was carried out for pipe 66 and the same conclusion was reached. Results can be found in Table 38 for pipe 36 and Table 37 for pipe 66.

Table 37. Variation in the composition of exposed pipe 66

Datafile	OIT (min)	Average OIT(min) (operator)	Variance	Average OIT(min)	Standard Deviation (operator)	Standard Deviation	T test
66-O@90 5400H VCC-JBT-1	6.00	5.5	2.0	6.4	1.4	1.3	0.184
66-O@90 5400H VCC-JBT-1	3.49						
66-O@90 5400H VCC-JBT-3	5.81						
66-O@90 5400H VCC-JBT-4	6.74						
66-O@90 5400H VCC-JBT-1 NZ	4.81	6.8	2.6		1.6		
66-O@90 5400H VCC-JBT-2 NZ	7.13						
66-O@90 5400H VCC-JBT-3 NZ	6.7						
66-O@90 5400H VCC-JBT-4 NZ	8.74						
66-O@90 5400H VCC-NZ-1	7.23	6.8	0.6		0.7		
66-O@90 5400H VCC-NZ-2	5.92						
66-O@90 5400H VCC-NZ-3	6.35						
66-O@90 5400H VCC-NZ-4	7.51						

Table 38. Variation in the composition of exposed pipe 36

Datafile	OIT (min)	Average OIT(min) (operator)	Variance	Average OIT(min)	Standard Deviation (operator)	Standard Deviation	T test
36-O@90 5400H VCC-JBT-1	8.34	8.5	0.1	9.6	0.3	1.4	0.005
36-O@90 5400H VCC-JBT-2	8.89						
36-O@90 5400H VCC-JBT-3	8.17						
36-O@90 5400H VCC-JBT-4	8.53						
36-O@90 5400H VCC-JBT-1 NZ	7.38	9.2	1.6		1.3		
36-O@90 5400H VCC-JBT-2 NZ	10.4						
36-O@90 5400H VCC-JBT-3 NZ	9.49						
36-O@90 5400H VCC-JBT-4 NZ	9.48						
36-O@90 5400H VCC-NZ-1	9.95	11.1	0.7		0.8		
36-O@90 5400H VCC-NZ-2	11.3						
36-O@90 5400H VCC-NZ-3	11.1						
36-O@90 5400H VCC-NZ-4	11.9						

There were no changes to the OIT of the outside for pipe 36 and pipe 57 after being exposed for 5400 hours to a 90°C water environment.

Pipe 58 is an HDPE pipe and as it was shown previously; this pipe material is pretty stable compared to the Aldyl A pipe. Therefore it was not surprising when comparing repeats

of the OIT test on the outside surface after almost 12000 hours at 90°C that a very low standard deviation (0.6 minutes) was seen. Also a general diminution in the OIT results was noticed at the end of the exposure work at 90°C. In conclusion the HDPE was the only material responding positively to the ageing work.

Table 39. Variation in the composition of exposed pipe 58

Datafile	Mass (mg)	OIT (min)	Average OIT(min) (operator)	Variance	Average OIT(min)	Standard Deviation (operator)	Standard Deviation
58-O@90 11997H VCC-NZ-1	5.4	1.8	2.6	0.3	2.6	0.6	0.6
58-O@90 11997H VCC-NZ-2	5.5	2.6					
58-O@90 11997H VCC-NZ-3	5.4	2.9					
58-O@90 11997H VCC-NZ-4	5.3	3.1					

3.2.3 TGA

The OIT results were questioned because two oxidation reactions were noticed when testing the tan pipes, see Figure 62. The second oxidation was more significant than the first and for this reason it was chosen to be reported rather than the first oxidation. The first reaction was attributed to the oxidation of an unstable additive when put in contact with oxygen at high temperatures. It was important to find out if the OIT results reported were true or if an additive was interfering with the actual OIT of the sample.

The thermogravimetric analyser (TGA) was the first proposed choice of instrument to overcome this issue. The TGA works out characteristics such as thermal stability of polymers. The temperature dependences of the sample mass at continuously increasing temperature are determined with the help of this method. A schematic representation of a thermogravimetric curve is showed in Figure 18. In order to estimate the thermal stability of a polymer, the temperature of onset of thermal degradation can be determined by the point of intersection of tangents to two branches of the thermogravimetric curve.

3.2.3.1 Thermogravimetric analysis – heating scan

Using TGA, the sample was heated at a continuous rate in an oxygen environment in order to compare the onset degradation values. From there a ranking was generated. For the

ranking, it was important to compare the tan pipe with reference pipes of known OIT. One green yellow Aldyl A pipe and one bright yellow modern pipe were chosen as references. The samples were prepared in the same way as OIT samples in order to eliminate any variable, with only the middle surface analysed.

The 5 mm diameter flat disks were heated from 25 to 900°C at 10°C/min under 50 ml/min oxygen gas flow. One green yellow pipe 36 and three tan Aldyl A (68, 117 and 165) were analysed. The OIT values obtained for the same surfaces analysed with the DSC instrument can be seen in Table 40.

The OIT ranking is as follows: 117<36<68<165. Crompton[66] defined that oxidative degradation in three stages for polyethylene: the first, up to about 350°C; the second, from 350°C to about 390°C; and the third, from 390°C to 455°C. He identified that the weight loss for the first stage could be smaller due to the presence of antioxidants in the polymer. Up to 350 °C, the weight loss of the PE can be attributed to degradation at the branching point in the polymer molecule[67].

Previous research highlighted that the degree of branching and the amorphous content would directly relate to the oxidation rate of polyethylenes. In other words the oxidation rate increases with the degree of branching. The differences in the rate of weight losses at other stages may also be due (at least in part) to changes in PE morphology during oxidation as stated by Luongo[68].

The Pyris software would not show the derivation curve results in %/°C as in Crompton's work but in %/min. However, a derivative curve in %/°C or in %/min would give the same results as the calculation uses the scan rate to convert the time to temperature. The first temperatures measured are taken during the first stage when antioxidants are consumed. These temperatures will be used for the ranking. In Table 40, the temperature obtained with the TGA against the OIT for the same surface analysed can be seen. The ranking obtained with the first onset on the TGA thermogram was: 165A< 68 E<117< 36.

Table 40. Oxidation induction time using the TGA instrument

Sample data file	TGA OIT – method 1 (min)	TGA OIT – method 2 (min)	OIT (min)
36-7A M OIT TGA	7.31	25.3	10.0[1]
68 A1 M OIT TGA	1.15	35.1 and 140	96.5[2]
117D M OIT TGA	0.75	13.75	0.26[3]
165 M OIT TGA	0.99	121.9	141
6803 M OIT TGA	No oxidation	No oxidation	more than 3 hours

1- Mean of 6 values
2- Mean of 4 values
3- Mean of 3 values

The polymer degradation for 117 is expected to happen earlier than for the other samples because the material is heavily degraded. However, this is not happening here. It seems from the TGA results that pipe 36 is more degraded than pipe 117. From there it becomes understandable that a ranking is not possible using this method. It seemed that the polymer degradation was more dependent on the polymer structure than to the antioxidants present.

Replication of the OIT method using the TGA instrument may be more suitable to understand the behaviour of the tan samples. It was decided to analyse a green yellow Aldyl A (pipe 36), three tan Aldyl A (pipes 68, 117 and 165) and one bright yellow PE80 (6803) sample using the same sampling conditions as one would do with when conducting OITs but with the TGA instrument.

3.2.3.2 Thermogravimetric Analysis – isothermal scan

During oxidation the polymer would gain weight. The reason for this was that the

antioxidants and the polymer would uptake oxygen molecules in such a way that alkanes would be oxidized into primary alcohols, alcohols would then be oxidized into aldehydes and finally aldehydes into carboxylic acids.

A PE80 with an OIT higher than 180 minutes was analysed for comparison with a green yellow sample that had a low OIT value (approximately 10min), pipe 36.

A weight gain was seen for the PE80 but no weigh loss following this. The TGA results obtained are in accordance with the OIT results. After 3 hours of testing under oxygen the weight started to stabilise indicating that a weight loss would be imminent. The sample was inspected at the end of the test. When a polymer degrades it usually goes to a brown colour. There was no colour change in the PE 80 after three hours of testing under oxygen.

The TGA thermogram for pipe 36 showed a different pattern. A small weight gain then a weight loss probably due to the introduction of oxygen was noticed around 14 minutes. Then there was a more noticeable weight gain followed almost immediately by an important weight loss. The sample was heavily degraded (dark brown colour) then taken out of the furnace. It was unclear at first how the oxidation induction time was meant to be calculated. Two methods were proposed:

- To take the intersection of the tangent to the first curve showing the weight loss (which was suspected to be an indicator of oxygen invading the system) with the tangent to the weight gain curve.

-To take the intersection of the tangent to the weight gain curve (which an indicator of the oxidation taking place) with the tangent to the weight loss following the gain (which indicate that the polymer is been combusted).

From both the values obtained the period spent under nitrogen (13.75 minutes) was subtracted in order to get an OIT value by TGA comparable to an OIT value by DSC. When comparing both calculation methods to the TGA second calculation method seemed to be the most appropriate.

The OIT value of pipe 68 at the middle position can vary by up to 15 minutes around the circumference of the pipe. Although this is a worst case scenario and the samples for OIT and TGA were taken close to each other the OIT might also be varying considerably at close positions. The results obtained by TGA are comparable to the results acquired by DSC, in other words the ranking is the same. One extra oxidation happened for pipe 68 at an earlier

time (35.1 minutes after the introduction of the oxygen). However if this effect is due to the bump characteristic of the tan sample it would also be expected for pipe 165, where such behaviour was not seen. However it should be kept in mind that pipe 165 and 68 are not made of the same material. Pipe 117 showed the shortest OIT values from calculations determined by the TGA and by the DSC.

In conclusion, the OIT values obtained with the DSC seems to be representative however it seems that the composition of the material can affect the oxidation. The OIT thermograms of tan pipe material all showed bumps, potentially due to cross linking. The OIT method by TGA shows a rather important weight gain followed by a weight loss before the actual oxidation of the polymer for pipe 68.

3.3 Hydro-thermal ageing

3.3.1 Pipe selection

It was decided to conduct thermal ageing in water at prescribed temperatures (with just the outer surface exposed) on a selection of different Aldyl A grade pipes see Table 41. Pipes samples available in sufficient length were chosen for this research. The size of the bath did not allow to have them all tested at once and the order in which they tested was a function of when they were excavated.

Table 41. Summary of Pipe selected for thermal ageing

Exova Code	Hydro thermal ageing start	Colour	Identification
3205 036-1A	January 2012	green yellow	Alathon 5043 – 2nd version
3205 057	January 2012	green yellow	Alathon 5043 – 2nd version
3205 066A	January 2012	green yellow	Unique material
3205 119A	August 2012	green yellow	Alathon 5043 – 2nd version
3205 150	August 2012	green yellow	Alathon 5043 – 2nd version
3205 161A	August 2012	green yellow	Alathon 5043 – 2nd version
3205 058	February 2012	pale yellow	HDPE 1
3205 068E	January 2012	Tan	Alathon 5043 – 2nd version
3205 117A	February 2012	Tan	Unique material
3205 165A	August 2012	Tan	Alathon 5040

3.3.2 OIT monitoring

The OIT values for the green yellow unexposed samples were generally less than 20 min. Therefore samples were regularly taken out the bath for testing at an average of 300 hours. After the first 1000 hours it became clear the OIT depletion did not happen as fast as anticipated consequently the intervals at which OITs were recorded decreased. No replicate samples were tested. The error associated with OIT measurement has been rigorously analysed in Section 3.2.2. Whilst there are location related variations on the pipe, the samples for hydro-thermal ageing were all cut from the same area, therefore location related variation will be minimised.

3.3.2.1 OIT monitoring of the tan coloured Aldyl A

The OIT value for the unexposed 3205 117 sample was below 5 minutes on the outside surface of the pipe. During the ageing process its OIT reached values above 25 minutes at 90°C. The monitoring at different ageing temperatures also showed an increase but to lower value (10-15 minutes), as shown in Figure 63.

The OIT value for the unexposed 3205 165 sample was around 45 minutes on the outside surface of the pipe. During the ageing process its OIT reached values above 100 minutes at 90°C and below 20 minutes at 60°C. The monitoring at 70°C also showed low OIT values below 30 minutes while the monitoring at 80°C showed high OIT values above 80 minutes, as shown in Figure 64.

Overall the Alathon 5040 shows large OIT variation. The 3205 165A pipe showed the highest variations. It is too early to tell definitively what is causing these variations however large variability was seen in OITs before ageing and so this could be related to the positions where samples were taken along the pipe length and around the pipe circumference.

The 3205 68 had high OIT values on the outside surface, around 80 minutes as shown Figure 68. The value rose noticeably during ageing to up to 140 minutes at 90°C. However, it is believed that after 3500 hours of exposure to a 90°C water environment the OIT should have been reaching lower values.

3.3.2.2 OIT monitoring of the green yellow coloured Aldyl A

For the Alathon 5043 samples 36, 57, and 66 used in the ageing programme the original OIT on the outside surface was low (10-12 minutes). For all samples shown in Figure 65, Figure 66 and Figure 67 the OIT values during ageing fluctuated between 10 and 20 minutes. These variations are due to the material being variable within its composition. However it is believed that after 3500 hours of exposure to a 90°C water environment the OIT should have been reaching values close to zero.

For the pipes 3205 119 and 161A, the original OIT on the outside surface was around 12 minutes as shown in Figure 69 and Figure 70Figure 71. The value was lower, around 6 minutes, for pipe 3205 150 as shown in Figure 70. While the OIT values of the samples exposed to 60, 70 and 80°C tend to stay low (below 12 minutes); the OIT of exposed samples at 90°C rose to 18 minutes.

3.3.2.3 OIT monitoring of the pale yellow coloured HDPE

The original OIT on the outside surface was around 14 minutes as shown in Figure

72. After ageing for 9000 hours the OIT value is finally lowering to zero.

3.3.2.4 Summary

The OIT data obtained at 80 °C and most particularly 90 °C showed the most unexpected trends in terms of increased OIT as ageing time increased. This indicates the possibility of diffusion of stabilisers / stabilising species to the area where they are most needed.

Preliminary headspace GC-MS studies have revealed that the green yellow sample 36 contained dissolved alkanes which are also found in natural gas. This suggests that mercaptans would be present within the pipe wall. Whilst the level of mercaptan in the pipe wall is below the limit of detection of the column/detector used, it is possible to smell it during machining operations on the pipes. The role of the mercaptan having a synergistic stabilisation effect with the stabilisers added should not be over looked in further work. The alkanes which dissolve in the pipe material may also be oxidised in preference to the polyethylene and may therefore sacrificially protect the pipe.

The Alathon 5043 and 5040 did not react to the ageing as expected and this is because their material composition was variable originally. Possible reasons for this would be that the polymer may have been protected by the mercaptan an alcane molecules traveling in the pipes. Pipe 117 and 66 reacted the same way as the Alathon 5040 and 5043 to the exposure work. Therefore it is concluded that the remaining lifetime determination of the Aldyl A material is not possible by monitoring the antioxidant depletion because of the variable nature of the material. On the other hand the pale yellow HDPE material, which was stable relatively to its composition originally, reacted as expected to the ageing work. Therefore, it can be concluded that the lifetime determination through antioxidant depletion method is only suitable for material which shows consistent OIT data implying homogenous distribution of stabilisers.

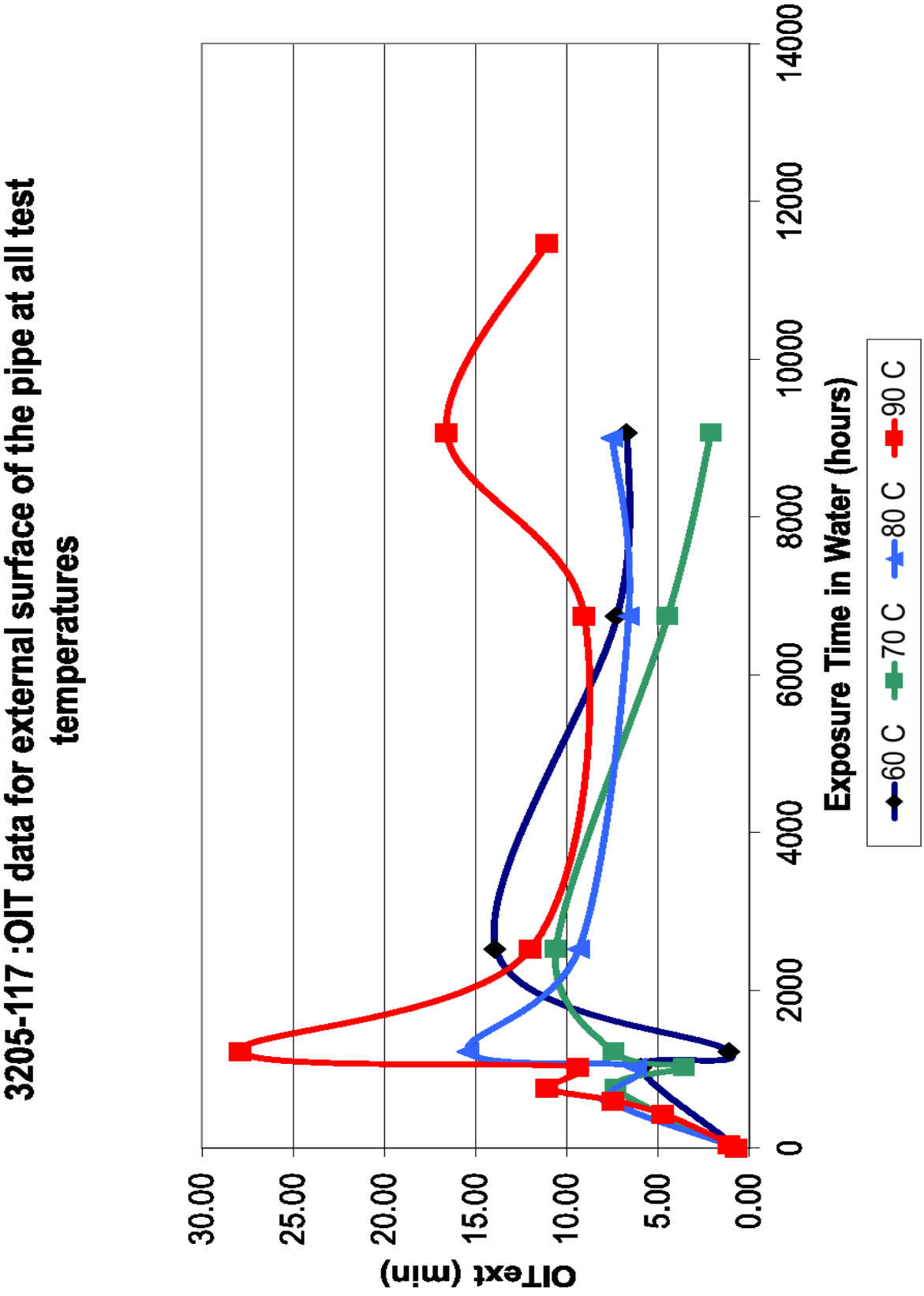


Figure 63. OIT depletion monitoring at the external surface of pipe 3205 117 at different ageing temperatures.

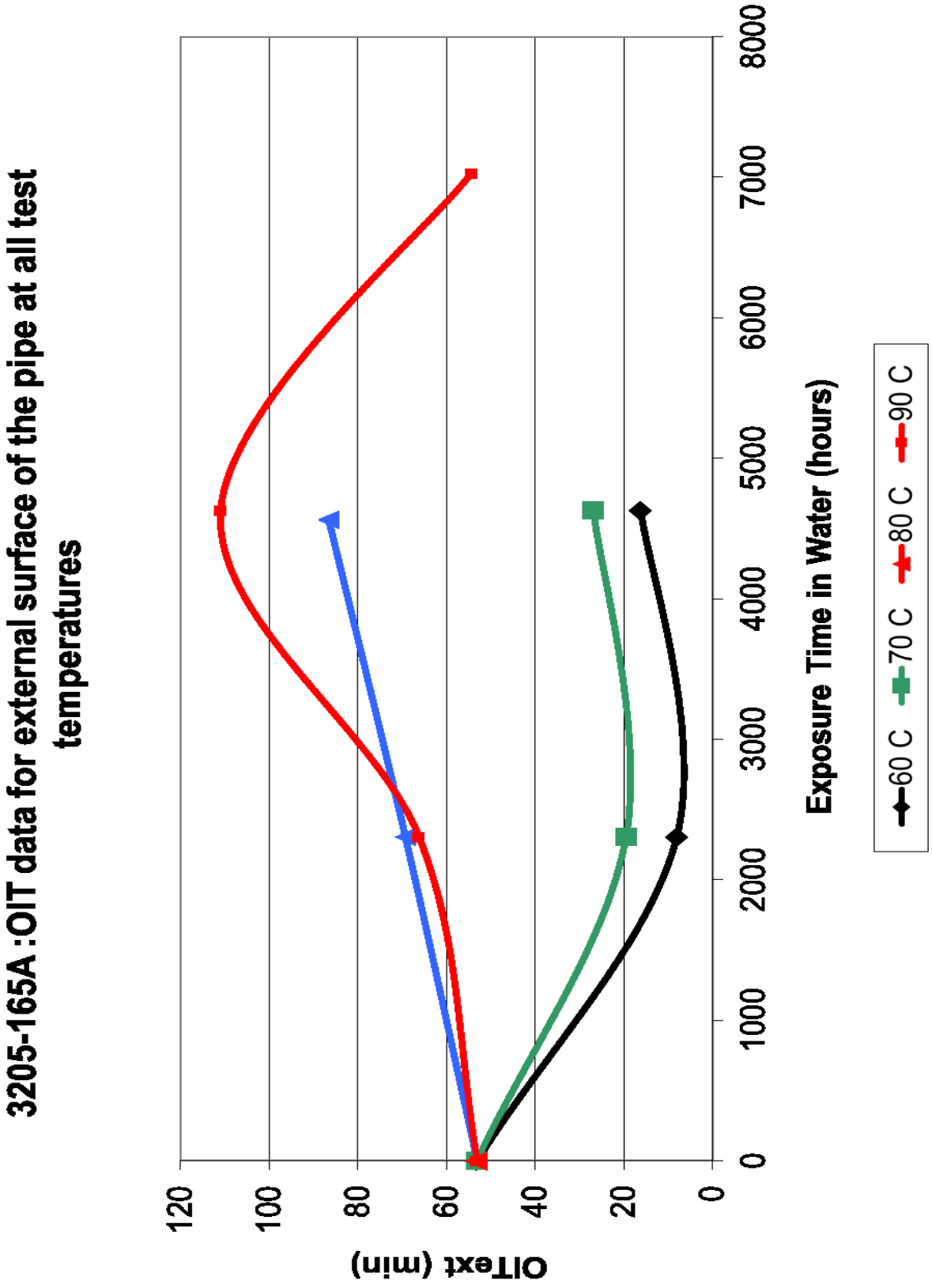


Figure 64. OIT depletion monitoring at the external surface of pipe 3205 165A at different ageing temperatures.

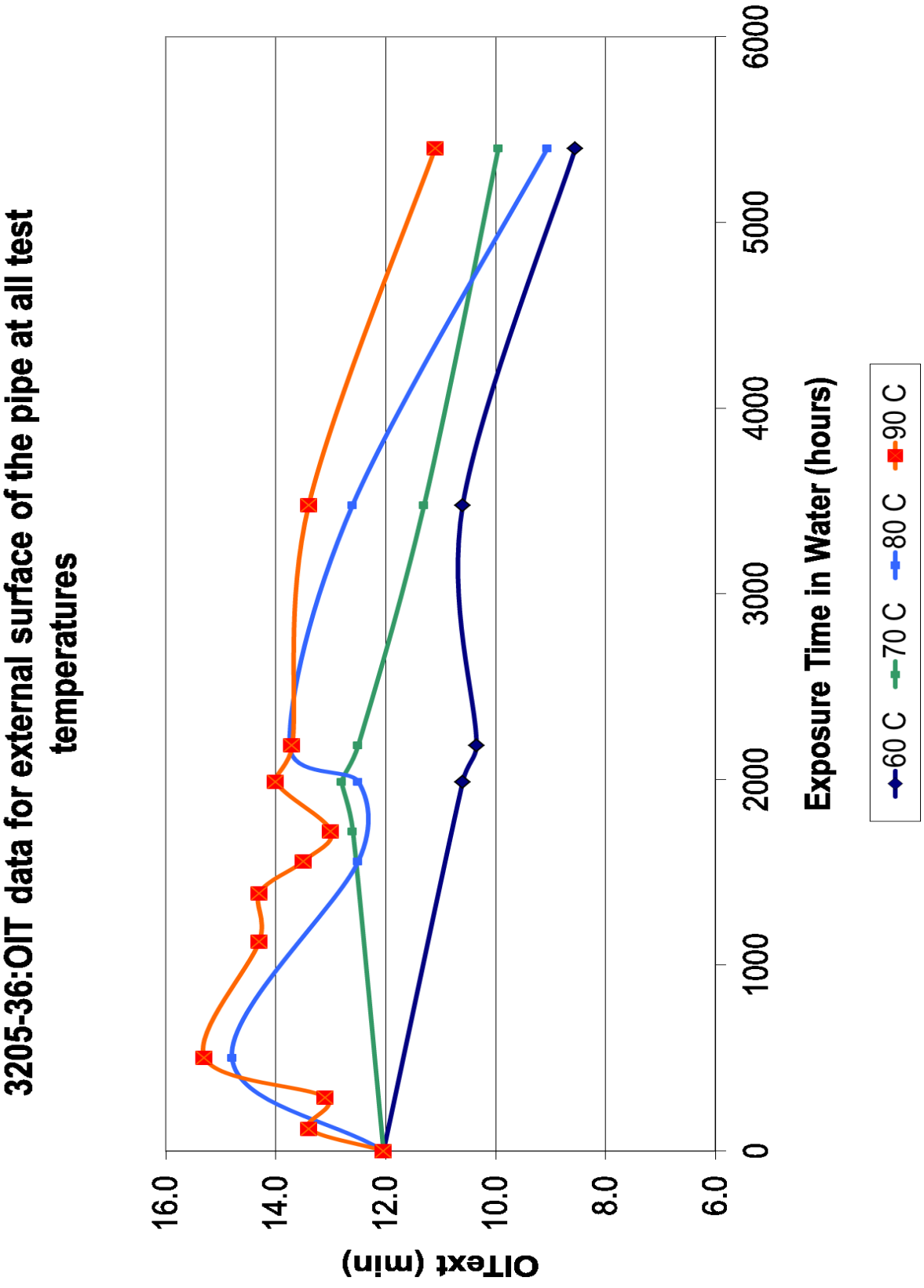


Figure 65. OIT depletion monitoring at the external surface of pipe 3205 36 at different ageing temperatures.

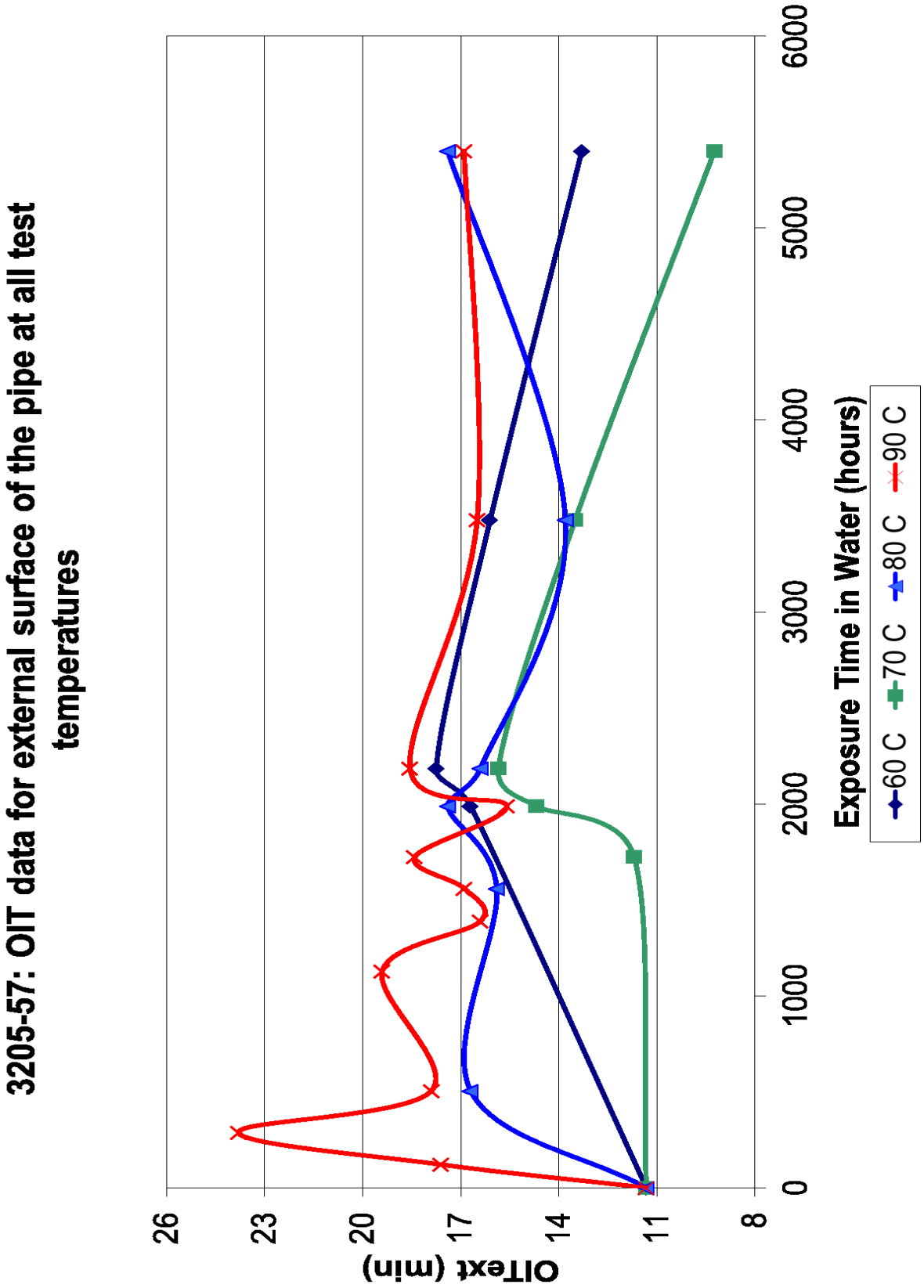


Figure 66. OIT depletion monitoring at the external surface of pipe 3205 57 at different ageing temperatures.

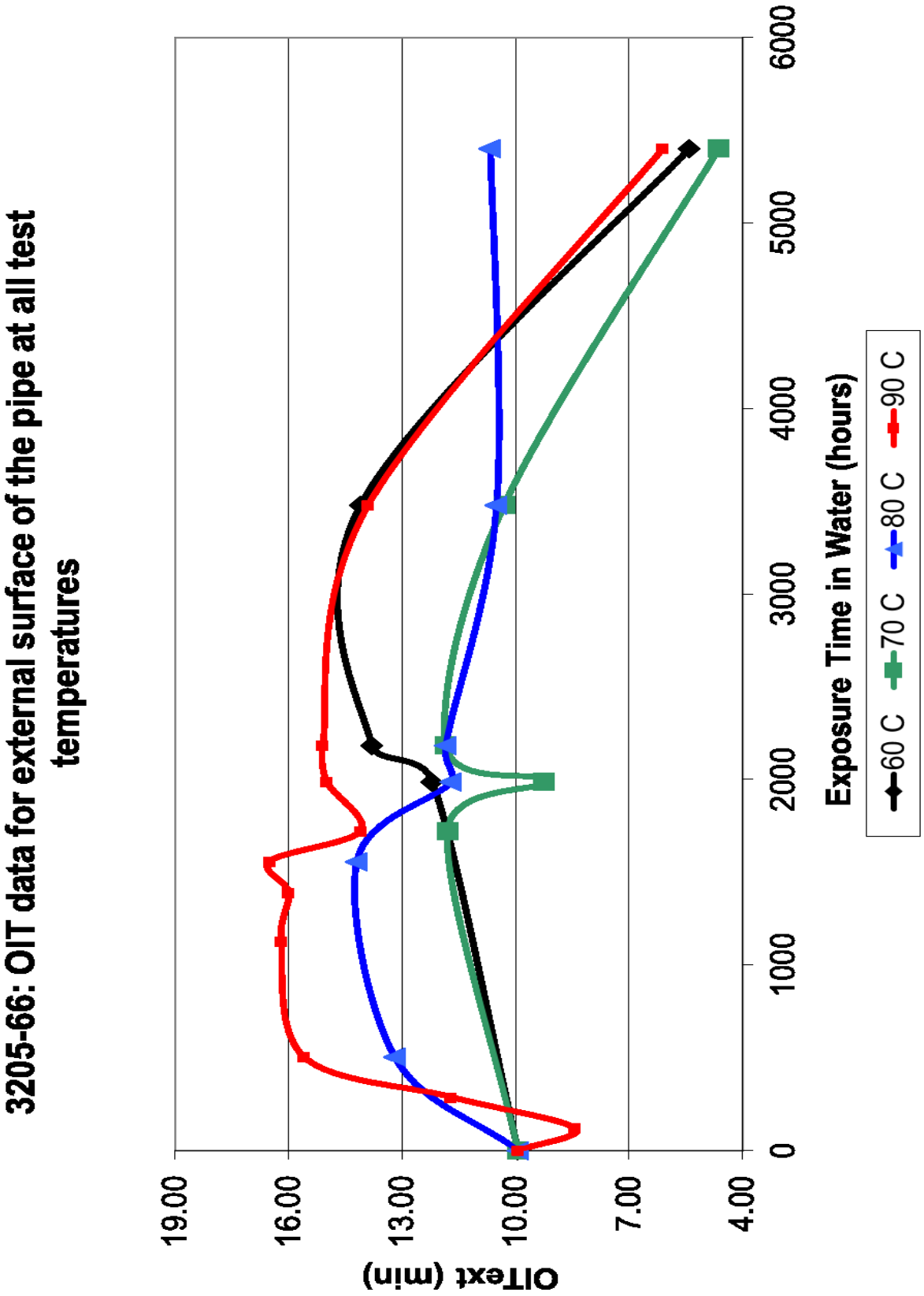


Figure 67. OIT depletion monitoring at the external surface of pipe 3205 66 at different ageing temperatures.

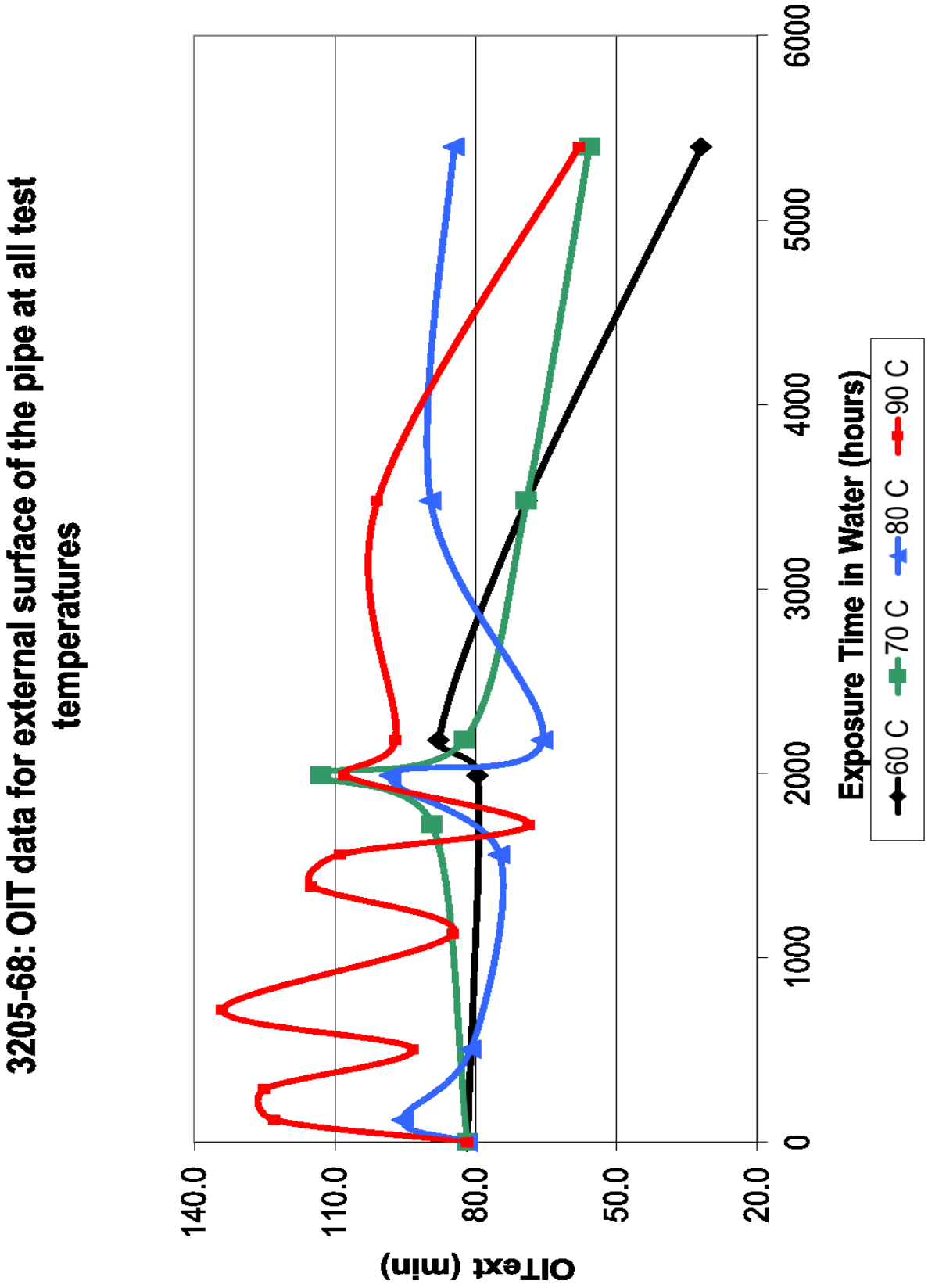


Figure 68. OIT depletion monitoring at the external surface of pipe 3205 68 at different ageing temperatures.

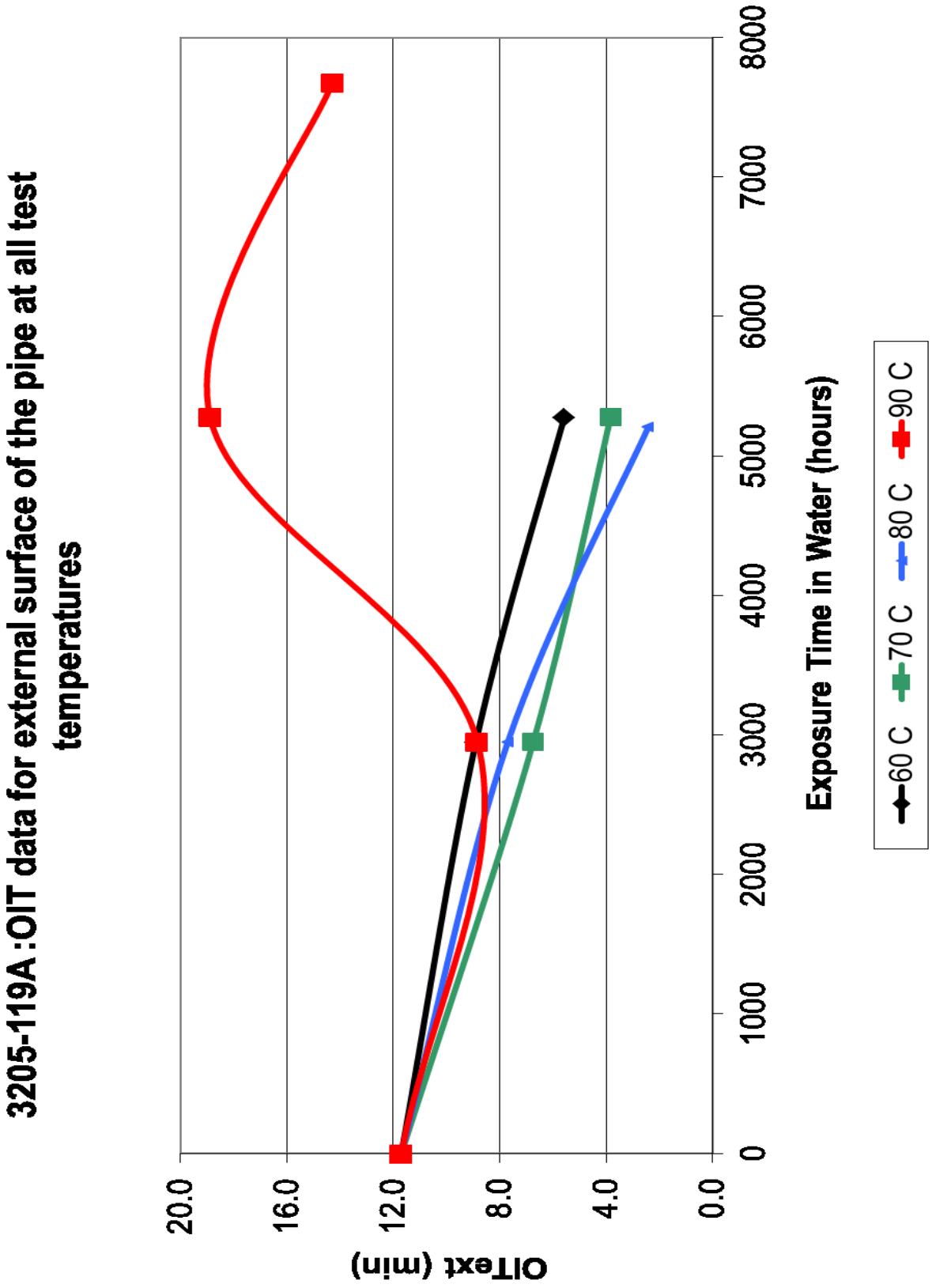


Figure 69. OIT depletion monitoring at the external surface of pipe 3205 119A at different ageing temperatures.

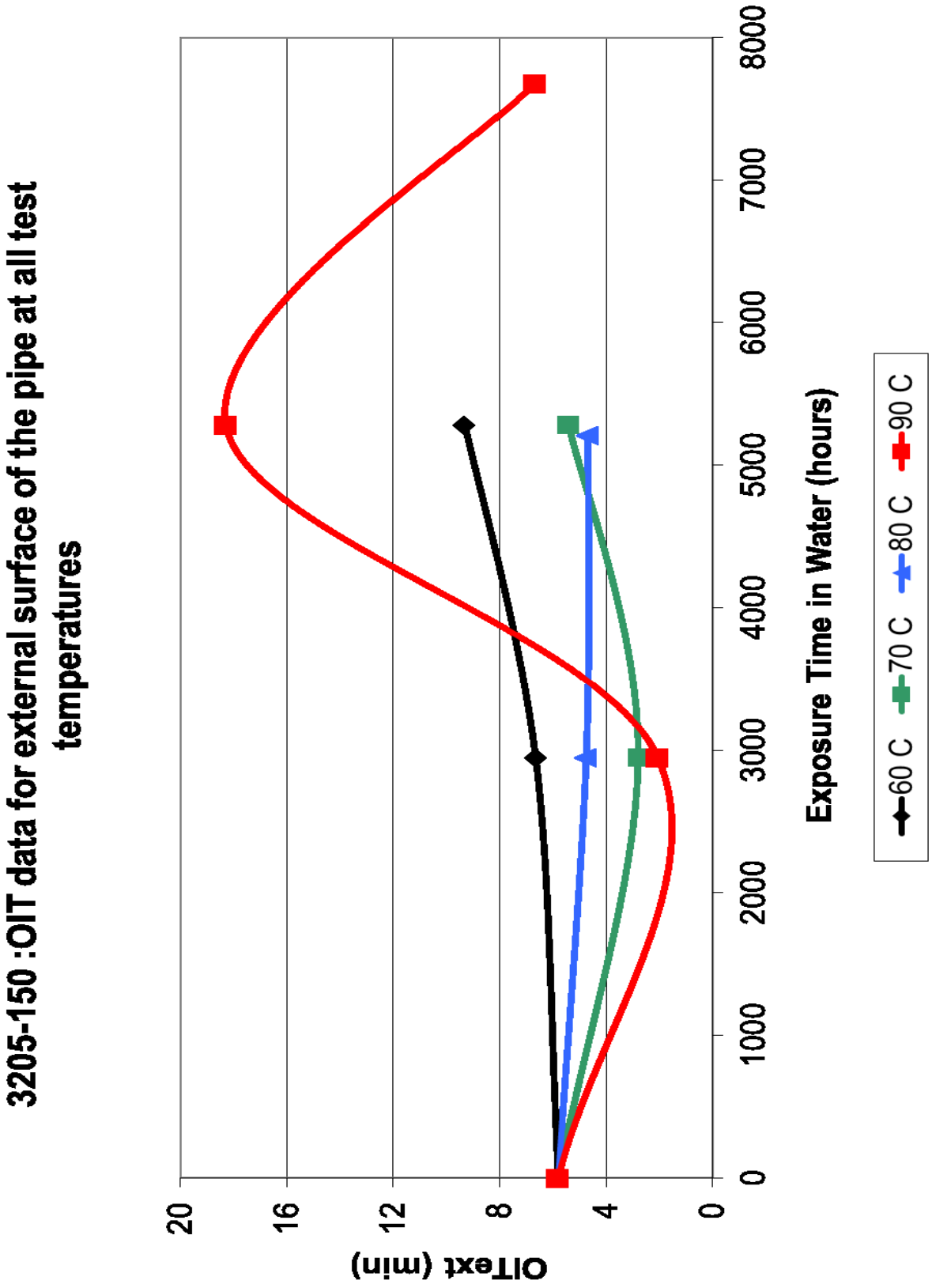


Figure 70. OIT depletion monitoring at the external surface of pipe 3205 150 at different ageing temperatures.

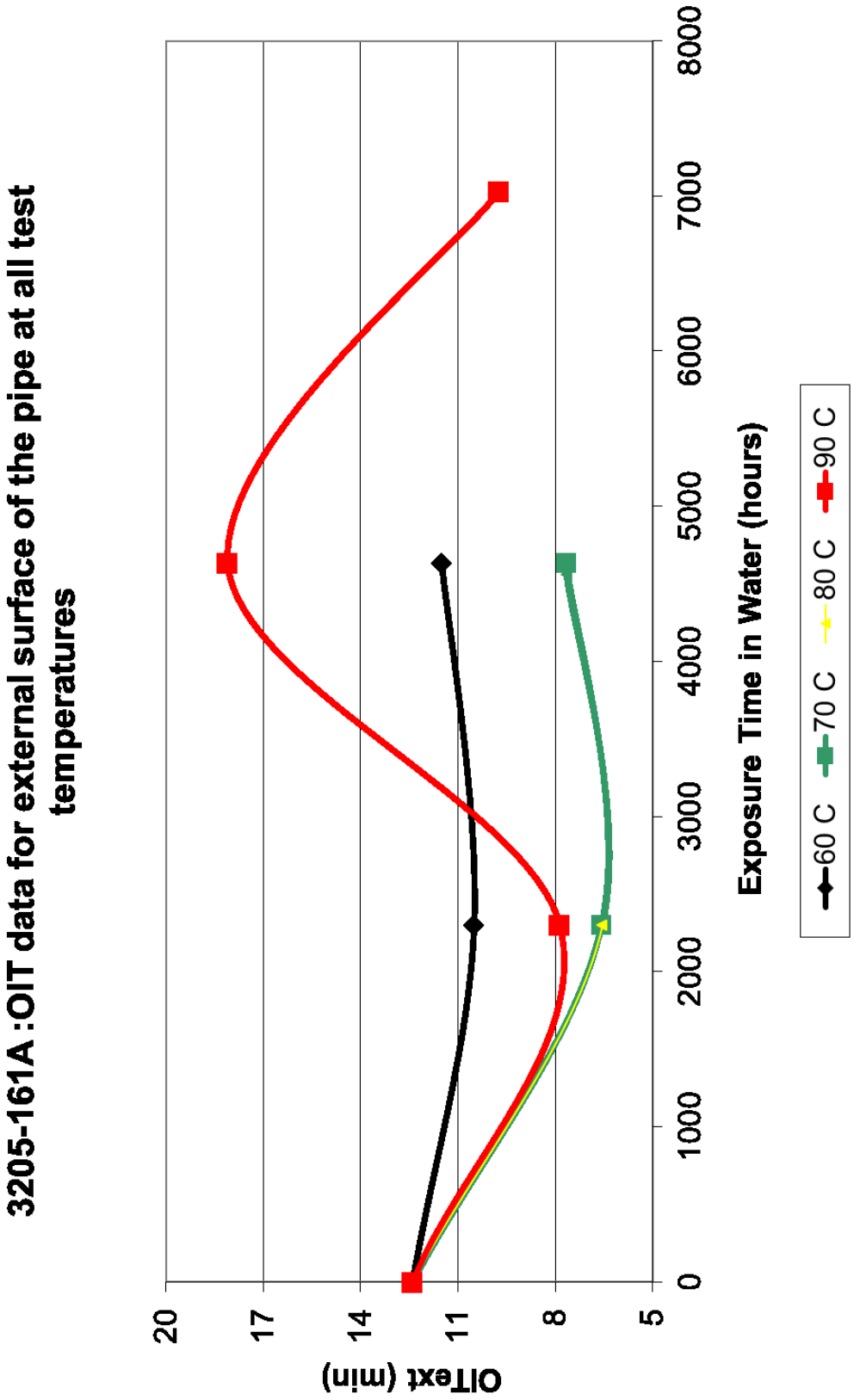


Figure 71. OIT depletion monitoring at the external surface of pipe 3205 161A at different ageing temperatures.

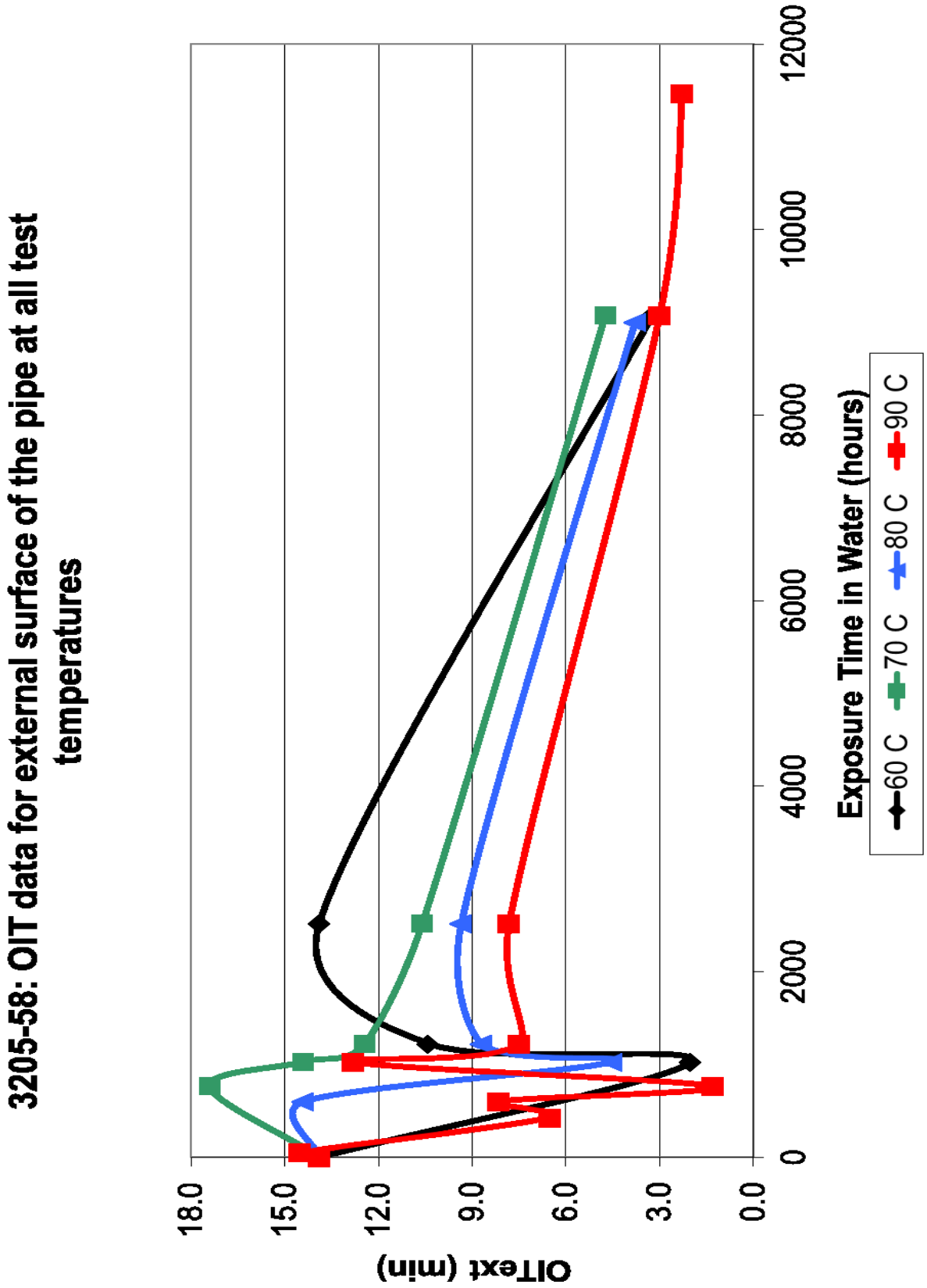


Figure 72. OIT depletion monitoring at the external surface of pipe 3205 58 at different ageing temperatures.

4 Chapter IV: Conclusions

This work has successfully identified the PE materials installed during the 1970's in the UK gas distribution networks. The identification work was carried out using the recently introduced SIS method with the novel addition of using the first derivative of the SIS data. This operation improved peak resolution, and has enabled creation of a library of historic PE pipe materials. Hence the differentiation between different PE type (MDPE and HDPE) is easily conducted. More challenging differentiation between different grades within the same class of PE is also greatly facilitated. The creation of a library database is cost-effective and time saving for the client as only one test is required to identify the pipe material. The testing can be carried out directly on pipe shavings, therefore no need to remove the pipe from the ground.

SIS overcomes the limitations associated with MFR and density techniques. SIS was able to resolve the unique materials that were created as part of manufacturing trials. These materials could not have been differentiated through MFR and density tests because their values were falling within expected ranges.

The SIS technique is not affected by the processing condition of the material because they are erased before the start of the annealing process. Therefore factors such as processing conditions, pipe diameters will not affect the SIS results. Quench cooling does not seem to affect the SIS either because differences in SIS thermograms were not observed when comparing bore and outside surfaces of the pipes. However, the area under the SIS curve should be determined to see if the difference in crystalline content comes through. When comparing the SIS thermograms of the aged sample to the unaged nothing was found. It may be that degradation has no effect on SIS results or that the pipes were not degraded enough to show any difference. This must be investigated further.

The first method of identification of the Alathon grade was through the determination of their MFR and density. The Alathon 5040 and 5043 were easily differentiated because of their recognisable melt flow rate properties. The Alathon 5040 is less viscous (2 g/10min) than the Alathon 5043 (1.2 then later 1.1 g/10min). However, the two versions of the

Alathon 5043 could not be identified using MFR or density measurements.

The Alathon 5040 was identified using information such as the pipe colour, MFR, density results, as well the SIS curve shape, verifying the use of SIS as an identification technique for these materials.

Using the SIS curve shape it was possible to isolate clearly the two versions of the Alathon 5043 featuring different MFR values.

Materials such as the tan samples from the USA (49A, 50, 51 and 52), the green yellow aldyl A pipe 66 and the tan Aldyl A pipe 117 were identifiable using the SIS curve shape. Pipes 66 and 117 are believed to be the result of manufacturing trials leading to the creation of new pipe materials. The MFR and density values for these pipes are in accordance with the Alathon 5043 (second version) for the green yellow pipe and the Alathon 5040 for the tan pipe. Therefore the individuality that these pipes demonstrated through SIS could not have been seen using MFR and density tests.

The green yellow metric pipes 11 and 53A were found to be made of a different material. They are probably also result of manufacturing trials.

In conclusion the SIS technique can be used to identify pipe material after years in service. However, it is preferable to use the first derivative of the SIS curve in order to achieve improved resolution of peaks. The SIS is not particularly sensitive to the degradation or the material may not have reached sufficient degradation to be detected using the SIS technique. The library database produced can be used in the future to identify materials after years in service, and this is also applicable to modern PE material.

The viability of FTIR as a method for the characterisation of the level of oxidation, and hence remaining life time of, aged pipe is questionable because the method used (ATR) could not resolve degradation on the outside surface of the tan pipe 117. OIT measurements indicated that the latter sample is missing antioxidants. ATR-FTIR spectra revealed sharp but weak carbonyl peaks mostly on the bore surfaces of certain samples. This led to the supposition that the peaks could be assigned to the blooming of stabilisers and other additives instead of degradation.

The extensive work conducted on the unexposed tan, green yellow and pale yellow samples prior to the ageing work led to the conclusion that the pale yellow pipes materials were the more consistent in terms of composition. The tan and green yellow material showed

variable OIT results through the pipe wall, length and circumference, potentially due to use of the masterbatching production process.

The Alathon 5043 and 5040 did not react to the ageing as expected because of the high variability studied in the unaged samples. Thus the residual lifetime determination of the Aldyl A material is not possible by antioxidant depletion for these materials. The pale yellow material gave more predictable OIT behaviour toward the end of the ageing but originally started off with variable OIT results. Therefore it is not certain if the remaining lifetime can be determined for the HDPE material, however this must be investigated in further work.

This work was based on previous successful studies[1]. However the conditions to which the pipes were exposed are different. Previously a modern blue HDPE material, classified as PE100 was subjected to water ageing for residual lifetime determination via antioxidant depletion. The pipe had not been in service prior to the testing but was intended for drinking water application. Therefore, the pipe surfaces were all aged in the same way to reproduce the field conditions. The antioxidant package was also fully known at the start of the work. There are too many variable to compare and understand why the study on the old Aldyl A gas pipe did not work as intended.

The chemical study revealed that the pipes were still in good condition because polymer degradation had not started. However, the pipes should be taken out of service before they reach this stage. Therefore a suitable analytical method must be found to predict when the material will reach the stage of polymer degradation. As this has not been found during the course of this study, mechanical testing should be used instead to give information about the pipe current conditions.

5 Chapter V: Further Work

The SIS technique must be studied in depth in order to understand which factors which can affect the curve shape and to what extent. Factors such as extreme degradation should be investigated. This time the work should be conducted on PE material with a more consistent composition. Perhaps this could be done using modern PE water pipe.

The crystalline content and the area under the SIS might be linked; therefore in further work it would be interesting to compare SIS thermograms of the same grade with increasing crystalline content. Because the crystalline content is directly linked to the density of the material it may be worth comparing it to the first two as well. If a linear relationship is found when plotting the data, it will become possible to determine the density and crystalline content of the material without having to conduct extra testing. This will give even more credit to the SIS technique.

Furthermore, changes in crystalline content are also sign of degradation in the polymeric material. Therefore if a relationship is found, one could extrapolate the effect of degradation on the SIS curve shape or area under the curve.

The innovative way of analysing the data should be extended to modern materials of more complex composition such as bimodal PE material. The SIS derivative analysis can detect double peaks where only one is showing when analysing via the normal SIS analysis. This suggested that the derivative analysis was able two distinct lamellaes with very close thicknesses. A SIS library for new materials should be produced using the SIS derivative analysis. This will ease identification in the future and allow degradation studies to take place.

The carbonyl peak is only visible via FTIR when polymer degradation has started. Polymer degradation starts well after the pipes have reached the end of their service life. Therefore the development of an analytical technique to identify the end of life of PE gas pipes is required.

A suitable lifetime determination method must still be found for the Aldyl A material. This method will probably involve mechanical testing as the chemical testing as failed for

these materials.

The antioxidant depletion technique could also be used on exhumed “modern” gas pipes where the dispersion of stabiliser is more even throughout in order to properly identify the differences in behaviour between gas and water pipes. If a difference is found it might confirm the sacrificial role of the gas and gas additives in terms of stabilisation of the pipes.

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